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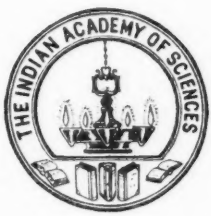

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ON A PROBLEM OF THE TETRAHEDRON.

By K. Venkatachaliengar.

(From the Department of Mathematics, University of Mysore.)

Received March 12, 1938.

(Communicated by Prof. B. S. Madhava Rao.)

The problem of the existence and the bounds of the volume of the tetrahedron the areas of whose faces are given has been raised by A. Narisinga Rao.* It is clear from the well-known maximum property of the sphere that there must be an upper bound. It is surprising to find that the lower bound is zero, *i.e.*, given any $\epsilon > 0$ we can deform any given tetrahedron in such a way that its volume is $< \epsilon$, while the areas of its faces remain the same as before. The problem can be easily generalised to higher dimensions. I shall first of all prove the results for three dimensions and indicate the generalisation later. In a paper published elsewhere in this issue Prof. K. S. K. Iyengar has given an analytical investigation. I have proceeded more from a geometrical point of view and have thus been able to discover the interesting theorem that the tetrahedron of maximum volume is an orthogonal one.

1. Let ABCD denote the tetrahedron and Δ_a, Δ_b, Δ_c, Δ_d denote the areas of faces BCD, CAD, ABD and ABC. Let us take $\Delta_a \leqslant \Delta_b \leqslant \Delta_c \leqslant \Delta_d$. If the Δ's are given the necessary and sufficient condition for the existence of tetrahedra is that

$$(1)\quad \Delta_a + \Delta_b + \Delta_c \geqslant \Delta_d.$$

The equality sign occurring only when it is a plane quadrilateral. Let λ, μ, ν be the angles which the first three faces make with the fourth. Then from elementary geometry it is clear that (2) the sides of the ΔABC must be proportional to $\Delta_a \sin\lambda$, $\Delta_b \sin\mu$, $\Delta_c \sin\nu$, while

$$(3)\quad \Delta_d = \Delta_a \cos\lambda + \Delta_b \cos\mu + \Delta_c \cos\nu.$$

In order that the tetrahedron exists there must be a real solution for λ, μ and ν. The necessity of (1) is obvious. I prove the sufficiency as follows :

Take λ to be a sufficiently small positive angle, and $\mu = \angle PQR$, $\nu = \angle PRQ$, where PQR is a triangle having $PQ = \Delta_b$, $PR = \Delta_c$ and $QR = \Delta_d - \Delta_a \cos\lambda$. The conditions for the existence of this triangle are $\Delta_b + \Delta_c \geqslant \Delta_d - \Delta_a \cos\lambda$ and $\Delta_d + \Delta_b \geqslant \Delta_c + \Delta_a \cos\lambda$. The former

* *The Mathematics Student*, June 1937, 5, No. 2, 90.

will be satisfied if λ be small enough and the latter is automatically satisfied. If λ decreases, $\Delta_d - \Delta_a \cos\lambda$ decreases and hence $\mu + \nu$ increases. Therefore $\Delta_b \sin\mu = \Delta_c \sin\nu$ must increase. Therefore by making λ still smaller we can have $\Delta_a \sin\lambda < \Delta_b \sin\mu = \Delta_c \sin\nu$. If, for *e.g.*, μ be obtuse λ can be so taken as to make μ a right angle. This proves the existence of real tetrahedra with the required conditions. [In case there is equality sign in (1), $\lambda = \mu = \nu = 0$ and the problem reduces to a trivial plane-geometry-problem.) The analysis given here can automatically be generalised to higher dimensions. Instead of taking a small λ and then determining μ and ν from the method indicated, we take in the case of n-dimensions the first $(n-2)$ angles to be small enough and proceed in exactly the same way.

2. I now obtain an expression for the upper bound. Let a, b, c be the sides of the triangle ABC and h the height of the tetrahedron through D. Then

$$(4)\quad a \leqslant \frac{2\Delta_a}{h},\quad b \leqslant \frac{2\Delta_b}{h},\quad c \leqslant \frac{2\Delta_c}{h}.$$

If a, b, c vary subject to (4) it is easy to prove from elementary considerations that the area of the triangle is maximum if $a = \frac{2\Delta_a}{h}$, $b = \frac{2\Delta_b}{h}$, $c = \frac{2\Delta_c}{h}$, in case these can form an acute-angled triangle and in any case (including the preceding) the area of the triangle formed by them must be less than

$$\frac{2\Delta_a\Delta_b}{h^2}.$$

$\therefore\quad \Delta_d < \frac{2\Delta_a\Delta_b}{h^2}$ or if V be the volume of the tetrahedron $V^2 < \frac{4}{9}\Delta_a\,\Delta_b\,\Delta_d$.

It must be noted here that we have not taken Δ_d to be the largest of the Δ's. In fact we can take Δ_d to be the smallest area, *i.e.*, the upper bound for the volume is

$$\frac{\sqrt{2}}{3}\,[\text{the product of the three least areas}]^{\frac{1}{2}}.$$

This upper bound is attained if $\Delta_d^2 = \Delta_a^2 + \Delta_b^2 + \Delta_c^2$. If ABCD be the tetrahedron the angles at the corner D are all right angles. This is easily generalised to higher dimensions with a corresponding expression for the upper bound. In the case of three dimensions in case the numbers Δ_b, Δ_c, Δ_d can form the lengths of sides of an acute-angled triangle with area Δ_0, then

$$V^2 < \frac{4\Delta_a\Delta_0}{9}.$$

3. We now come to the case of the lower bound and the problem of geometrically characterising the tetrahedra with the maximum volume.

It is easy to prove by differentiation using Lagrange's method of multipliers that the maximum can only be attained when the tetrahedron is orthogonal, *i.e.*, when every pair of opposite sides are perpendicular to each other; but the following method gives us a visual way of realising how the lower bound is zero as well as the fact that the maximum occurs when it is orthogonal. Let PQ be the line of shortest distance between the opposite sides AB and CD of a tetrahedron ABCD. Let $PQ = d$, $PA = x_1$, $PB = x_2$, $PC = y_1$ and $PD = y_2$ and the angle between the sides be θ. Let the tetrahedron be deformed to another tetrahedron A'B'C'D' by means of the following transformation. A'B' and C'D' are perpendicular to each other. PQ is again the line of shortest distance. And

$$d' = \frac{d}{\sqrt{\sin\theta}},\ PA' = x_1\sqrt{\sin\theta},\ PB' = x_2\sqrt{\sin\theta},$$

$$PC' = y_1\sqrt{\sin\theta},\ PD' = y_2\sqrt{\sin\theta}.$$

The area of the faces of ABCD are easily seen to be

$$(x_1 - x_2)^2 (d^2 + y_1^2 \sin^2\theta),$$
$$(x_1 - x_2)^2 (d^2 + y_2^2 \sin^2\theta),$$
$$(y_1 - y_2)^2 (d^2 + x_1^2 \sin^2\theta),$$
$$(y_1 - y_2)^2 (d^2 + x_2^2 \sin^2\theta).$$

The areas of faces of A'B'C'D' are

$$\sin\theta\ (x_1 - x_2)^2 \left(\frac{d^2}{\sin\theta} + y_1^2 \sin\theta\right)$$
$$= (x_1 - x_2)^2 (d^2 + y_1^2 \sin^2\theta), \text{ etc.}$$

i.e., the areas do not change by means of the deformation and the volume increases; for the volumes of the two tetrahedra are $\frac{1}{6}(x_1 - x_2)(y_1 - y_2)\sin\theta$, and $\frac{1}{6}(x_1 - x_2)(y_1 - y_2)\sqrt{\sin\theta}$.

∴ If any two pairs of opposite sides are not perpendicular we can increase the volume. Given any tetrahedron we deform it in this way and make two opposite sides perpendicular to each other. Then we can apply the inverse transformation and make the angle between these two sides as near to zero as we like without altering the areas. If θ is the angle between them the volume will be multiplied by $\sqrt{\sin\theta}$ and hence the lower bound of the volume is zero.

Now I apply this deformation process to another pair of sides and make them perpendicular, increasing the volume but keeping the areas the same and then to another pair of sides if they are not perpendicular already and so on *ad infinitum*. It will be proved that for this sequence of operations the sides of the tetrahedron are bounded both above and below. For, if, on the contrary, $AB \to 0$ for a subsequence of these operations the perpendicular from A on $BCD \to 0$. In case $AB \to \infty$ the perpendicular from

C on it$\to$0. Therefore in both the cases the corresponding height of the tetrahedron tends to zero against the fact that the volume of the tetrahedron goes on increasing. Hence for a subsequence of these operations the tetrahedra tend to an orthogonal tetrahedron. It is probable that there is only one such tetrahedron. That it is so has been proved by K. S. K. Iyengar.†

5. In the case of higher dimensions there is no need to have an analogous transformation. The same transformation is enough. I discuss here the case of a 4-simplex the 3-dimensional volumes of its five faces being given and prove that the volume will be maximum in case it is orthogonal, *i.e.*, when every one of its 4-dimensional faces is orthogonal. Let ABCDE be the simplex. Let Ee $= h$, be the perpendicular dropped to ABCD. Let V_a, V_b, V_c, V_d be the volumes of BCDE, ACDE, ABDE, and ABCE, X, Y, Z, W, the volumes of BCDe, $\cdots\cdots$, etc., and Δ_a, Δ_b, Δ_c, Δ_d the areas of faces of the tetrahedron ABCD. Then it is easy to see that

$$(5)\quad V_a^2 - \tfrac{1}{9}\,\Delta_a^2\,h^2 = X^2, \cdots\cdots\cdots \text{etc.},$$

and $X \pm Y \pm Z \pm W = V =$ the volume of ABCD.

Now suppose that the tetrahedron ABCD is not orthogonal. Then with the same Δ_a's we can form an orthogonal tetrahedron whose volume is ρV, where $\rho > 1$. Hence we can lessen the Δ_a's proportionately so that the volume of the orthogonal tetrahedron is again V. Then the set of equations (5) will be satisfied with an increased h. Therefore this deformation gives us a simplex of greater volume ; we can then apply the same to tetrahedra which are not orthogonal and so on as before. In this case also we prove that the sides are bounded both below and above. For if, say EB$\to\infty$. Then $h\to\infty$ against the fact that the volume goes on increasing. The two dimensional areas of all its 2-simplexes are bounded ; for

$\Delta_a^2 < V_a^2/h^2$ and h goes on increasing, etc. $\therefore$ If, say DB$\to\infty$ the height from C on the opposite 3-simplex which is less than the height from C on DB must tend to zero against hypothesis. Hence a subsequence of the sequence of these operations exist such that the 5-simplexes tend to a definite orthogonal 5-simplex.

Now we can multiply the Δ_a's by k, a quantity as great we please and divide h by the same quantity and construct a tetrahedron ABCD with these increased areas of faces and with the same volume as before. This is possible as the lower bound of the volume of the tetrahedron with fixed areas of faces is zero. The 5-simplex thus obtained will have a volume which is $\frac{1}{k}$ times the former. Hence the lower bound of the volume is zero.

† See § 6 in the paper by K. S. K. Iyengar, elsewhere in this issue.

DERIVATIVES OF 1-HYDROXY-2-NAPHTHOIC ACID.

Part IV. Compounds Derived from 4-Nitro-1-hydroxy-2-naphthoic Acid and Its Methyl Ether.

By S. N. Rao.

(From the Organic Chemistry Laboratories, Royal Institute of Science, Bombay.)

Received March 22, 1938.

(Communicated by Dr. T. S. Wheeler, Ph.D., F.Inst.P., F.I.C., M.I.chem.E.)

In continuation of the previous work,[1] the nitration of methyl 1-hydroxy-2-naphthoate and its methyl ether has now been studied. Direct nitration of the hydroxy acid gives mostly 2 : 4-dinitro-1-naphthol ; the direct nitration of the methoxy acid can be effected, however, at low temperature.[2] The hydroxy acid was nitrated by Konig[3] through intermediate sulphonation. The nitro-group in both the cases was found to enter in the 4-position. The nitration of the methyl esters is smooth and convenient. Methyl 1-hydroxy-2-naphthoate has been nitrated by Einhorn and Pfyl,[4] who, however, did not study its contsitution.

The acids obtained from the nitrated esters yielded the respective *naphthoyl chlorides* with phosphorus pentachloride. Various *derivatives* of these acids have been prepared from the naphthoyl chlorides.[5]

The work is being extended.

Experimental.

Methyl 4-nitro-1-hydroxy-2-naphthoate.—Nitric acid (d. 1·42 ; 5 c.c.) in acetic acid (10 c.c.) was slowly added at room temperature to methyl 1-hydroxy-2-naphthoate (12 g.) in acetic acid (120 c.c.). The nitro-ester separated in yellow needles. The resultant mixture was diluted with water and filtered (14 g.). Pale yellow needles from acetic acid ; m.p. 159–60°. (161°, Einhorn and Pfyl, *loc. cit.*).

[Found : N (micro), 5·7 ; $C_{12}H_9O_5N$ requires N, 5·7 per cent.]

4-Nitro-1-hydroxy-2-naphthoic acid.—The above ester (10 g.) was heated with alcoholic sodium hydroxide (100 c.c.; 2 N ; rectified spirit 30 c.c.) for two

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[1] *J. Ind. Chem. Soc.*, 1936, **13**, 609, 645.

[2] Froelicher and Cohen, *J.C.S.*, 1922, 1657.

[3] *Ber.*, 1890, **23**, 806 ; *cf.* Schmitt and Burkard, *Ber.*, 1887, **20**, 2699.

[4] *Ann.*, 1900, **311**, 63.

[5] See *J. Ind. Chem. Soc.*, *loc. cit.*

hours on the water-bath. The acid obtained on acidification (7 g.) crystallised from acetic acid in thick pale yellow needles, m.p. 212–14° (decom.) (212°, Konig, *loc. cit.*).

[Found : N (micro), 5·9 ; $C_{11}H_7O_5N$ requires N, 6·0 per cent.]

2 : 4-dinitro-1-naphthol, m.p. 138–39°, was obtained on heating the acid (1 g.) in acetic acid (15 c.c.) with nitric acid (d. 1·42 ; 2 c.c.) in acetic acid (4 c.c.) ; the mixed m.p. with an authentic sample showed no depression.

4-*Nitro*-1-*hydroxy*-2-*naphthoyl chloride*.—The clear solution obtained on heating a mixture of the nitro-acid (2 g.), phosphorus pentachloride (4 g.) and dry benzene (6 c.c.) on the water-bath, was filtered and dry petroleum ether (10 c.c.) was added to the filtrate. The ***naphthoyl chloride*** which slowly separated in yellow needles was filtered and dried over phosphorus pentoxide under reduced pressure, m.p. 132–33°.

[Found : Cl, 14·4 ; $C_{11}H_6O_4NCl$ requires Cl, 14·1 per cent.]

Methyl 4-*nitro*-1-*methoxy*-2-*naphthoate*.—Solutions of methyl 1-methoxy-2-naphthoate from methyl 1-hydroxy-2-naphthoate (20 g.)[6] in acetic acid (solution made up to 80 c.c.) and nitric acid (d. 1·42 ; 8 c.c.) in acetic acid (8 c.c.) were mixed and heated on the water-bath for fifteen minutes. The *nitro-ester* (14 g.) separated on cooling and crystallised from methyl alcohol in pale yellow needles, m.p. 110–11°.

[Found : N (micro), 5·5 ; $C_{13}H_{11}O_5N$ requires N, 5·4 per cent.]

4-*Nitro*-1-*methoxy*-2-*naphthoic acid*.—The above ester (14 g.) was heated on the water-bath with alcoholic sodium hydroxide (60 c.c. 2 N ; rectified spirit 100 c.c.) for half an hour. The acid (8 g.) obtained on acidification crystallised from rectified spirit in pale yellow needles, m.p. 196–97°. (195–96°, Froelicher and Cohen, *loc. cit.*)

[Found : N, 5·8 ; $C_{12}H_9O_5N$ requires N, 5·7 per cent.]

4-Nitro-1-hydroxy-2-naphthoic acid (confirmed by mixed m.p.) was obtained, when the methoxy acid (1 g.) in acetic acid (5 c.c.) was heated with hydriodic acid (d. 1·5 ; 6 c.c.) for 10 minutes. The mixture was kept overnight and the solid obtained on dilution crystallised from acetic acid in thick pale yellow needles, m.p. 212–14° (decom.).

4-*Nitro*-1-*methoxy*-2-*naphthoyl chloride*.—The clear solution obtained on heating, on the water-bath, a mixture of the nitro acid (2 g.), phosphorus pentachloride (2 g.) and dry benzene (6 c.c.) was filtered and treated with dry petroleum ether (25 c.c.). The ***naphthoyl chloride*** which slowly separated

[6] *J. Ind. Chem. Soc.*, 1936, **13**, 645.

Derivatives of 4-nitro-1-hydroxy-2-naphthoic acid.

Name	Formula	M.P.	Appearance	Solvent	Nitrogen analysis (micro)	
					Found	Required
1. Phenyl ester ..	$C_{17}H_{11}O_5N$	159–60°	Thick pale yellow needles	Acetic acid	4·6	4·5 per cent.
2. Ethyl ester ..	$C_{13}H_{11}O_5N$	103–4°	Flat pale yellow needles	Rectified spirit	5·4	5·4 „ „
3. Anilide ..	$C_{17}H_{12}O_4N_2$	231–2° (decom.)	Silky needles	Acetic acid	9·2	9·1 „ „
4. *o*-Toluidide ..	$C_{18}H_{14}O_4N_2$	201–2° (decom.)	Thick pale yellow needles	„ „	9·2	8·7 „ „
5. *m*-Toluidide ..	$C_{18}H_{14}O_4N_2$	236–37°	Silky pale yellow needles	„ „	8·6	8·7 „ „
6. *p*-Toluidide ..	$C_{18}H_{14}O_4N_2$	258–9°	„	„ „	8·6	8·7 „ „
Derivatives of 4-nitro-1-methoxy-2-naphthoic acid.						
7. Phenyl ester ..	$C_{18}H_{13}O_5N$	114–15°	Pale yellow needles	Rectified spirit	4·5	4·3 per cent.
8. Ethyl ester ..	$C_{14}H_{13}O_5N$	101–2°	Long pale yellow needles	Dil. alcohol	5·1	5·1 „ „
9. Anilide ..	$C_{18}H_{14}O_4N_2$	170–1° (decom.)	Pale yellow needles	Benzene	8·9	8·7 „ „
10. *o*-Toluidide ..	$C_{19}H_{16}O_4N_2$	175–6°	„	Acetic acid	8·5	8·3 „ „
11. *m*-Toluidide ..	$C_{19}H_{16}O_4N_2$	138–40°	Thick pale yellow needles	Benzene + pet. ether	8·7	8·3 „ „
12. *p*-Toluidide ..	$C_{19}H_{16}O_4N_2$	164–5°	Pale yellow needles	Acetic acid	8·6	8·3 „ „

in yellow needles, was filtered and dried over phosphorus pentoxide under reduced pressure, m.p. 103–4°.

[Found : Cl, 13·3 ; $C_{12}H_9O_4NCl$ requires Cl, 13·4 per cent.]

The author thanks Dr. T. S. Wheeler and Mr. N. W. Hirwe for their helpful suggestions and keen interest in the work and Dr. Nazir Ahmad for granting him various facilities.

THE ELECTRO-STATIC FORCES AND THE ELASTICITY CONSTANTS.

By B. Y. Oke.

(From Sir Parashurambhau College, Poona.)

Received March 19, 1938.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

Suppose an ionic lattice consists of equally spaced neutral planes, the equilibrium distance separating these being d. For simplicity, let the x-axis be taken perpendicular to the planes and the planes be numbered $j = \cdots -3, -2, -1, 0, 1, 2, 3, \cdots$. If $\phi(x_j)$ denotes the potential per unit area of the jth plane relative to only one particular plane, say the plane $j = 0$, then U, the energy density of the crystal is given by :

$$U = \frac{1}{2d} \sum_j \phi(x_j). \tag{1}$$

We assume a deformation by which the distance between consecutive planes is uniformly changed. If x_j is the distance of the jth plane from the plane $j = 0$, we have

$$x_j = dj\,(1 + x_x)\,; \tag{2}$$

x_x being the elongation per unit length in the direction of the x-axis.

The expression (1) for the energy density may be developed as :

$$U = \frac{1}{2d} \sum_j \left\{ \phi(dj) + djx_x \left(\frac{\partial\phi}{\partial x}\right)_{x=dj} + \tfrac{1}{2}\, d^2j^2x_x^2 \left(\frac{\partial^2\phi}{\partial x^2}\right)_{x=dj} + \cdots \right\}; \tag{3}$$

c_{11}^e, the contribution of the electro-static forces to the elasticity-constant along the direction of the x-axis, will be given by

$$c_1^e = \frac{d}{2} \sum_j j^2 \left(\frac{\partial^2\phi(x_j)}{\partial x^2}\right)_{x=dj}; \tag{4}$$

In two papers,[1] the formula for c_{11}^e, used by the author, contained the factor j instead of the correct factor j.[2] This error[2] crept in on account of the misinterpretation of the conception of stress in a lattice. The numerical calculations given in these two papers have been repeated in the light of the correct formula (4). As the formula effects only higher terms of the series representing the elasticity constant, the corrected formula is found to have small influence on the numerical results given in these two papers.

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[1] B. Y. Oke, *Proc. Ind. Acad. Sci.*, 1936, 4, 514 and 667.

[2] The error was brought to notice by the examiners of a dissertation submitted by the author.

C-ALKYL RESORCINOLS.

Part III. A Direct Synthesis of Rhizonaldehyde.

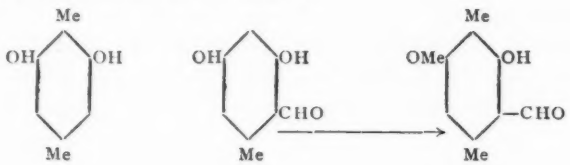
By R. C. Shah and B. V. Samant.

(From the Departments of Chemistry, Ismail College, Andheri, and Royal Institute of Science, Bombay.)

Received March 4, 1938.

Rhizonic acid, 3 : 6-dimethyl-4-methoxy-2-hydroxy-benzoic acid, one of the more important lichen acids, has been obtained as a degradation product of a number of lichen depsides like barbatic acid, atranorin, soloric acid and dirhizonic acid. The acid, and the corresponding aldehyde, rhizonaldehyde, 3 : 6-dimethyl-4-methoxy-2-hydroxy benzaldehyde (III), both of which contain the β-orcinol (2 : 5-dimethyl resorcinol) nucleus, have been synthesised by various workers by indirect methods which are long and cumbersome. The essential intermediate for the synthesis of rhizonaldehyde (III), has been β-orcinol (I), which is obtained either from *p*-xylene or *p*-xylidene through a number of stages,[1,2,3] or from ethyl 5-methyl-dihydroresorcylate, through 5-methyl-dihydroresorcinol, by successive stages of methylation, bromination and catalytic debromination in the presence of palladised calcium carbonate.[4] The β-orcinol is then converted by methylation and formylation by the Gattermann method into rhizonaldehyde.

We find that rhizonaldehyde can be conveniently synthesised in a remarkably simple manner directly from orcinol. Orcinol was converted into orcylaldehyde (II) and this on nuclear methylation by methyl alcoholic caustic potash and methyl iodide, readily afforded rhizonaldehyde (III) in fair yield (*cf.* Robinson and Shah[6]).



Experimental.

3 : 6-*Dimethyl-4-methoxy-2-hydroxy-benzaldehyde* (*Rhizonaldehyde*) (*III*).—The nuclear methylation of orcylaldehyde was carried out under conditions similar to those used by Robinson and Shah.[6] KOH (38 g., 6 mols.) was dissolved in hot methyl alcohol (170 c.c.) and orcylaldehyde (17 g., 1 mol.) added, which readily dissolved to a deep red solution. The mixture was cooled in ice water, and methyl iodide (42 c.c., 6 mols.) was added in one lot. After about 10 minutes, the separation of KI began to take place, after which it was kept at 0° for further three hours. The mixture was then taken out of the cooling bath, and after leaving overnight, refluxed gently for three hours, some more methyl iodide (25 c.c.) being added in two portions at intervals of one hour. Most of the methyl alcohol was then distilled off, on the water-bath, and the liquid concentrated at 100° in a porcelain basin. The residue was diluted with water and extracted with ether. The ether extract was washed with 50 c.c. of dilute NaOH (1N) five times. The first washing was rejected, and the remaining four washings, when acidified with hydrochloric acid, gave impure rhizonaldehyde (0·7 g.). The ethereal layer on evaporation gave crude rhizonaldehyde (2·5 g.) which was partially purified from a little alkali-insoluble matter by solution in alkali and reprecipitation by hydrochloric acid. The combined yield of the aldehyde was then crystallised twice from dilute alcohol, when it was obtained in fine colourless prisms, m.p. 136°. Robertson and Stephenson[3] and St. Pfau[5] give m.p. 136°. Yield 2·7 g. (Found : C, 66·4 ; H, 6·8 ; Calc. for $C_{10}H_{12}O_2$: C, 66·7 H, 6·7 per cent.). It gave a reddish brown coloration with alcoholic ferric chloride, and dissolved in dilute alkali only moderately easily.

The normal methylation production, the 4-methyl ether of orcylaldehyde, an expected bye-product in the reaction, was not isolated.

The Oxime.—A mixture of rhizonaldehyde (0·2 g.), KOH (0·03 g.), and hydroxylamine hydrochloride (0·1 g.) was refluxed in aqueous-alcoholic solution for three hours. The cooled mixture on dilution deposited the oxime as a whitish precipitate. It was collected and crystallised twice from alcohol and then from much water in small crystals, m.p. 187–89°. St. Pfau[5] gives m.p. 188–89°. (Found : C, 61·3 ; H, 6·5 ; N, 7·5. Calc. for $C_{10}H_{13}O_3N$: C, 61·5 ; H, 6·7 ; N, 7·2 per cent.)

Summary.

Rhizonaldehyde, 3 : 6-dimethyl-4-methoxy-2-hydroxy benzaldehyde, has been synthesised directly from orcinol. Orcinol was converted into

orcylaldehyde, and this on nuclear methylation by methyl-alcoholic KOH and MeI, afforded rhizonaldehyde.

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5. St. Pfau, *Helv. Chim. Acta.*, 1928, **11**, 864.
6. Robinson and Shah, *J.*, 1934, 1492.

A NOTE ON NARASINGA RAO'S PROBLEM RELATING TO TETRAHEDRA.

By K. S. K. Iyengar.

(*From the Department of Mathematics, University of Mysore.*)

Received March 12, 1938.

§ 1. *Introduction.*

A. Narasinga Rao[1] has raised the question, "The areas of the four faces of a tetrahedron are α, β, γ, δ. Is the volume determinate? If not, between what limits does it lie?

It may be mentioned at once that an upper bound must exist as is evident from Schwarz's isoperimetric inequality[2]

$$O^3 - 36\pi V^2 \geqslant 0$$

for convex surfaces; or again from Steinitz's inequality[3] relating to the volume of a tetrahedron of given surface area. Narasinga Rao's problem, however, is quite distinct from these isoperimetric problems since what is given here is not the total surface area, but that of the individual faces.

In the first place, I notice that the problem could be easily generalised to n-dimensions, and would then become,

"Given $(n+1)$ positive numbers, does a simplex in n-dimensions exist having for the $(n-1)$-dimensional volumes of its $(n+1)$ faces, the $(n+1)$ given numbers? If so what are the limits between which the nth-dimensional volume of the simplex lies?"

The analysis for n-dimensions is so similar to that in 3 dimensions that I have given here in most places the solutions for 3 dimensions, and, wherever necessary, mentioned the corresponding analysis and result for n-dimensions.

The principal results obtained are as follows for 3 dimensions:—

$$\text{Let} \quad \Delta_1 \leqslant \Delta_2 \leqslant \Delta_3 \leqslant \Delta_4;$$

(1) The necessary and sufficient condition for the existence of one tetrahedron at least is that the sum of the lowest three areas must be greater than the greatest area, *i.e.*,

$$\Delta_1 + \Delta_2 + \Delta_3 > \Delta_4.$$

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[1] *The Mathematics Student*, June 1937, 5, (No. 2), 90.

[2] Blaschke, *Integral geometrie*, Bd. 2.

[3] Steinitz, *Ency. Math. Wiss.*, Bd. 3, Teil 1, 2, S. 139.

(2) The lower bound of the volumes of all the tetrahedra having for its areas the given numbers is zero.

(3) The tetrahedron having the maximum volume under the given conditions is an orthogonal one[4] (*i.e.*, having opposite edges orthogonal) and is unique.

(4) The upper bound of the volume is given by

$$V \leqslant \left(2/9\ \Delta_1\Delta_2\Delta_3\right)^{\frac{1}{2}} \left\{1 - \frac{\Omega^2}{3\left(\Delta_1^2\Delta_2^2 + \Delta_2^2\Delta_3^2 + \Delta_3^2\Delta_1^2\right)}\right\},$$

where

$$2\,\Omega = \Delta_4^2 - \Delta_1^2 - \Delta_2^2 - \Delta_3^2, \text{ the equality holding if } \Omega = 0,$$

For n-dimensions, (1) and (2) can be generalised in a straightforward way. (3) also holds, but I have not been able to prove, by the methods given in this paper, that the tetrahedron is unique, although it is likely to be so. (4) can be replaced by

$$V \leqslant \left\{\frac{(\underline{n-1})^n}{(\underline{n})^{n-1}}\ \Delta_1\Delta_2 \cdots \Delta_n\right\}^{\frac{1}{n-1}} \cdot \left\{1 - \frac{\left(\Delta_{n+1}^2 - \sum_1^n \Delta_r^2\right)^2}{\frac{4 \cdot n\,(n-1)}{2}\left(\Sigma\,\Delta_r^2\Delta_s^2\right)}\right\}.$$

§ 2. *Fundamental Formulæ.*

Two formulæ easy to obtain are the most important in the following analysis and we will give them in the beginning.

Let $O \cdot\cdot P_1 \cdot\cdot P_2 \cdot\cdot P_n$ be the $\overline{n+1}$ points of a simplex, O being the origin. Let the Vector $OP_1 = R_1\,(l_{11} \cdot\cdot l_{12} \cdot\cdot l_{13} \cdot\cdot l_{1n})$ where l_{1r} are the direction cosines of the line OP_1, etc. Let the $\overline{n-1}$ dimensional volume of the face $(O, P_1P_2 \cdots P_{n-1})$ be Δ_n. If we call OP_1 the vector A_1. Then Δ_n will be proportional to the absolute value of the vector product

$$[A_1\,A_2 \cdot\cdot\cdot A_{n-1}], \textit{ i.e.,}\ \underline{|n-1} \cdot \Delta_n = |\,[A_1, A_2 \cdots A_{n-1}]\,|, \text{ etc.}$$

Let the direction cosines of the vector $[A_1\,A_2 \cdot\cdot A_{n-1}]$ be $l_{n1}, l_{n2} \cdots l_{nn}$. We will, for the sake of convenience, put $\bar{A}_n = [A_1 \cdot A_2 \cdots A_{n-1}]$, etc. Then if V be the volume of the simplex

$$\text{Then}\qquad V^{n-1} = \frac{(\underline{n-1})^n}{(\underline{n})^{n-1}}\ \Delta_1 \cdot \Delta_2 \cdot \Delta_n \cdot \begin{vmatrix} l_{11} & l_{12} & l_{1n} \\ l_{21} & l_{22} & \cdots \\ \cdot & \cdot & \cdot \\ l_{n1} & \cdots & l_{nn} \end{vmatrix} \qquad \text{I}$$

where $\Delta_1\ \Delta_2 \cdots$ are the $\overline{n-1}$ dimensional volumes of the faces at O. Indicating the angle between the vectors $\bar{A}_1$ and $\bar{A}_2$ by $\bar{\xi}_{12}$,

[4] This theorem is due to Mr. K. V. Iyengar. See his paper elsewhere in this issue.

The formula (I) could be written as :

$$V^{n-1} = \frac{(n-1)^n}{(\underline{n})^{n-1}} \Delta_1 \Delta_2 \Delta_n \begin{vmatrix} 1 & \cos \bar{\xi}_{12} \cos \bar{\xi}_{13} \cdots \cos \bar{\xi}_{1n} \\ \cos \bar{\xi}_{12} & 1 \quad \cos \bar{\xi}_{23} \cdots \cdots \\ \cdots & \cdots \\ \cos \bar{\xi}_{n1} & \cdots \cdots 1 \end{vmatrix}^{\frac{1}{2}} \qquad \text{I}'$$

Let Δ_{n+1} be the $\overline{n-1}$ dimensional volume of the face opposite O, *i.e.*, of the points $(P_1, P_2, \cdots P_n)$. Then by projection or otherwise it is easy to prove

$$\sum_1^n \Delta_r^2 + \sum_1^n \sum_1^n 2 \Delta_r \Delta_s \cos \bar{\xi}_{rs} = \Delta^2_{n+1}. \qquad \text{(II)}$$

So that the problem becomes (1) does there exist a solution of (II) at all in n-dimensions and what are the bounds of the determinant in (I′) under condition (II). We will hereafter restrict our analysis to 3 dimensions.

§ 3. *Question of Existence.*

Equation (II) becomes

$$\Delta_1^2 + \Delta_2^2 + \Delta_3^2 + 2\Delta_2\Delta_3 \operatorname{Cos} \bar{\xi}_{23} + 2\Delta_3\Delta_1 \operatorname{Cos} \bar{\xi}_{31} + 2\Delta_1\Delta_2 \operatorname{Cos} \bar{\xi}_{12} = \Delta_4^2. \qquad \text{(II}')$$

We will so choose the vertex O such that $\Delta_1 \leqslant \Delta_2 \leqslant \Delta_3 \leqslant \Delta_4$ (*i.e.*, opposite the largest area).

We will call $\bar{\xi}_{23} = x$, $\bar{\xi}_{31} = y$, $\bar{\xi}_{12} = z$. In order that a real tetrahedron may exist, we must have solution (II′) so that

$$\left.\begin{array}{ll} (1) & 0 \leqslant x \leqslant \pi,\ 0 \leqslant y \leqslant \pi,\ 0 \leqslant z \leqslant \pi. \\ (2) & x + y + z < 2\pi. \\ (3) & y + z > x,\ z + x > y,\ x + y > z. \end{array}\right\} \text{ R (region).}$$

Let $E = \sum_1^3 \Delta_r^2 + \Sigma\, 2\Delta_2\Delta_3 \cos x.$

The maximum value of E in R is $(\sum_1^3 \Delta_r)^2$.

(C) $\therefore \sum_1^3 \Delta_r > \Delta_4$ equality cannot occur because then the only solution, then, will be $x = 0 = y = z$, which will not be a tetrahedron. Therefore condition (C) is necessary.

At $x = \pi,\ y = \pi,\ z = 0$

$$E = (\Delta_1 + \Delta_2 - \Delta_3)^2. \qquad \text{In case } \Delta_1 + \Delta_2 > \Delta_3$$

then, since $\Delta_1 \leqslant \Delta_2 \leqslant \Delta_3$.

$$E < \Delta_1^2. \quad \therefore \quad < \Delta_4^2.$$

In case $\Delta_3 > \Delta_1 + \Delta_2$

$$E < \Delta_2^2. \quad \therefore \quad < \Delta_4^2.$$

$\therefore$ If $\Delta_1 + \Delta_2 + \Delta_3 > \Delta_4$ there are always solution of (II′) in the interior of R. |C|

The region R is as a matter of fact a tetrahedron. We can join the point (000) to the point $(\pi, \pi, 0)$ by a space curve L lying entirely in R. Except for end points. Since $E(000) > \Delta_4^2 > E(\pi, \pi, 0)$.

$\therefore$ Since E is continuous there exists at least one solution on L in the interior of R. Since we can draw infinity of such curves L, there are infinity of such tetrahedra. An entirely similar discussion holds for n-dimensions.

§ 4. *The Lower Bound.*

The points (000) and $(\pi, \pi, 0)$ are on the plane $z + x - y = 0$ in R.

$$E(000) = (\sum_1^3 \Delta_r)^2 \text{ and } E(\pi, \pi, 0) = (\Delta_1 + \Delta_2 - \Delta_3)^2.$$

$\therefore$ There are infinity of solutions of (II′) in the plane $z + x - y = 0$ in R. Consider the portion of the plane $z + x - y = \alpha$ in R, where α is a very small positive number. (We will call this α plane.) The maximum and minimum of E on this plane in the region R will be nearly the same as in the plane $z + x - y = 0$.

Since $E(000) > \Delta_4^2 > E(\pi, \pi, 0)$.

We easily see that there will be infinity of solutions of (II′) on this plane in the region R.

Now the determinant in I′ for this case is

$$\begin{vmatrix} 1 & \cos x & \cos y \\ \cos x & 1 & \cos z \\ \cos y & \cos z & 1 \end{vmatrix} = 4 \sin\left(\frac{x+y+z}{2}\right) \cdot \sin\left(\frac{y+z-x}{2}\right) \cdot \sin\left(\frac{z+x-y}{2}\right) \cdot \sin\left(\frac{x+y-z}{2}\right)$$

$$\therefore \quad \leqslant 4 \sin\left(\frac{z+x-y}{2}\right).$$

We therefore see that for all tetrahedra corresponding to solution in the plane (α) the $(\text{volume})^2 \leqslant 2/9\ \Delta_1 \cdot \Delta_2 \cdot \Delta_3 \cdot \sqrt{2\alpha}$. Therefore the lower bound of the volumes of the tetrahedra will be zero.

§ 5. *The Upper Bound.*

Coming now to the upper bound, we will take up the n-dimensional case. It is obvious that by the foregoing discussion, if (C) is satisfied there will be solutions for equation (II) in n-dimensions.

We therefore have to find the maximum of $\begin{vmatrix} 1 & \cos \xi_{12} \cos \xi_{13} \cdots \\ \cos \xi_{1n} \cdots & 1 \end{vmatrix} = D$

under $\sum_1^n \Delta_r^2 + 2\Delta_r\Delta_s \cos \xi_{rs} = \Delta_{n+1}^2$. Using the theory of Lagrangian Multipliers we get,

$$\frac{\begin{vmatrix} \cos \xi_{12} & \cos \xi_{23} & \cos \xi_{24} \cdots \\ \cos \xi_{31} & 1 & \cos \xi_{34} \\ \cos \xi_{41} & \text{cis } \xi_{43} & 1 \cdots \\ \cos \xi_{n1} & \cdots & 1 \end{vmatrix}}{\Delta_1 \cdot \Delta_2} = \text{similar terms.}$$

there being ${}^nC_2$ such terms.

Now let us designate the vector $L_{11}, L_{12} \cdots L_{1n}$ by L_1. Then it is easy to prove

$$\begin{vmatrix} \cos \xi_{12} & \cos \xi_{32} \cdots \\ \cos \xi_{13} & 1 \end{vmatrix} = \text{scalar product of the two vector products given by}$$

$[L_1, L_3, L_4, \cdots L_n]$ and $[L_2, L_3, \cdots L_n]$ $\therefore$ equal to $= [L_1 \cdot L_3 \cdots L_n][L_2 \cdot L_3 \cdots L_n]$.

$$= \frac{[\bar{A}_1 \bar{A}_3 \cdots \bar{A}_n] \cdot [\bar{A}_2 \cdot \bar{A}_3 \cdots \bar{A}_n]}{\{|\bar{A}_1| \cdot |\bar{A}_2| \cdots |\bar{A}_n|\}^2} \cdot |\bar{A}_1| \cdot |\bar{A}_2|$$

where $|A|$ indicates the absolute value of the vector A.

Let us call $D_* =$ the determinant $|A_1, A_2, \cdots A_n|$ and $D_* = |\bar{A}_1 \cdots \bar{A}_n|$.

Then the vector $[\bar{A}_1, \bar{A}_3 \cdot \bar{A}_4 \cdots \bar{A}_n] = D^{n-2} A_2$.

and $[\bar{A}_2 \cdot \bar{A}_3 \cdots] = D^{n-2} A_1$.

$$\therefore \begin{vmatrix} \cos \xi_{12} & \cos \xi_{23} \cdots \\ \cos \xi_{13} & 1 \cdots \end{vmatrix} = \frac{D^{2n-4} |\bar{A}_1| |\bar{A}_2|}{\{|\bar{A}_1| |\bar{A}_2| \cdots |\bar{A}_n|\}^2} \cdot (A_1 \cdot A_2)$$

$$= k \cdot \Delta_1 \cdot \Delta_2 \cdot (A_1 \cdot A_2).$$

Therefore the equations now become

$$R_1 R_2 \cdot (l_{11} l_{21} + l_{12} l_{22} + \cdots l_{1r} \cdot l_{2r} + \cdots) = R_p R_q \ (\Sigma \ l_{pr} l_{qr}) \qquad \text{(III)}$$

It is easy now to verify that opposite sides of the simplex are orthogonal. Take OP_1 and any side opposite $P_r P_s$. $(r \neq 1 \ s \neq 1.)$ The direction cosines of $P_r P_s$ are proportional to

$$(R_r l_{r1} - R_s l_{s1}), \quad (R_r l_{r2} - R_s l_{s2}), \text{ etc.}$$

Then for orthogonality we must have

$$l_{11} (R_r l_{r1} - R_s l_{s1}) + l_{12} (R_r l_{r2} - R_s l_{s2}) + \qquad = 0$$

i.e., $\sum_{k=1}^n R_r (l_{1k} l_{rk}) = \Sigma R_s (l_{1k} l_{sk})$, which is verified by equation (II).

Before we go to the discussion of the uniqueness of the orthogonal simplex having the specified volumes for its faces (the discussion being only for 3 dimensions), I should like here to obtain an expression for the upper bound of all the volumes of simplexes in n-dimensions.

Lemma :

Let $$\Delta_n = \begin{vmatrix} 1 & \cos \bar{\xi}_{12} \cos \bar{\xi}_{13} \cdots \cos \bar{\xi}_{1n} \\ \cos \bar{\xi}_{21} & 1 \\ \cos \bar{\xi}_{n1} & 1 \end{vmatrix}$$

We will call the minor of 1st term in the 1st row of Δ_n, Δ_{n-1} which is

$$= \begin{vmatrix} 1 & \cos \bar{\xi}_{23} \cdots \cos \bar{\xi}_{2n} \\ \cos \bar{\xi}_{23} & 1 \\ \cdot & \end{vmatrix} \text{ of order } (n-1).$$

We will call the minor of the last term in the last row of Δ_n as $\overline{\Delta}_{n-1}$

$$\text{which is } = \begin{vmatrix} 1 & \cos \bar{\xi}_{12} \cdots \cos \bar{\xi}_{1n-1} \\ \cos \bar{\xi}_{12} & \\ \cos \bar{\xi}_{1n-1} \cdots & 1 \end{vmatrix} \text{ of order } n-1.$$

We will call the minor of the 1st term in the first row of Δ_{n-1} as Δ_{n-2}

Then $$\Delta_n = \begin{vmatrix} 1 - \dfrac{\Delta_{n-1}}{\Delta_{n-2}} & \cos \bar{\xi}_{12} \cdots \cos \bar{\xi}_{1n} \\ \cos \bar{\xi}_{21} & \\ \cos \bar{\xi}_{n1} & 1 \end{vmatrix} + \frac{\Delta_{n-1}\,\overline{\Delta}_{n-1}}{\Delta_{n-2}}.$$

Now in the first expression the minor of the last term in the last row is zero and hence it is easy to prove that it is $= -$ (square of an expression).

$$\therefore \quad \Delta_n \leqslant \frac{\Delta_{n-1}\,\overline{\Delta}_{n-1}}{\Delta_{n-2}}.$$

We wish to prove that

$$\Delta_n \leqslant (1 - \cos^2 \bar{\xi}_{12})\ \Delta_{n-1}.$$

This is obviously true when $n = 2$, we will therefore assume to be true for $\overline{n-1}$ for such determinants and prove for n by induction.

Then $$\overline{\Delta}_{n-1} \leqslant (1 - \cos^2 \bar{\xi}_{12})\ \Delta_{n-2}.$$

$$\therefore \quad \Delta_n \leqslant (1 - \mathrm{Cos}^2\ \bar{\xi}_{12})\ \Delta_{n-1} \quad \text{by the above inequality.}$$

We therefore obtain $$\Delta_n < \sin^2 \bar{\xi}_{12} \cdot \cdots \cdot \sin^2 \bar{\xi}_{23} \cdots \sin^2 \bar{\xi}_{n-1 \cdot n}.$$

There are ${}_nC_2$ such terms. By suitably combining the terms by repeated operation of the above inequality, we get

$$\Delta_n{}^n \leqslant (\pi \sin^2 \bar{\xi}_{rs})^2.$$

By (I) we have

$$V^{n-1} = k. \begin{vmatrix} 1 & \cos \xi_{12} & \cdots \\ \cdots & \cdots & \cdots \\ \cdots & \cdots & 1 \end{vmatrix}^{\frac{1}{2}}.$$

$$= k \cdot \Delta_n^{\frac{1}{2}}.$$

$$\therefore \quad V^{\frac{n(n-1)}{2}} = k^{\frac{n}{2}} \Delta_n^{\frac{n}{2}}.$$

$$\therefore \qquad V = k^{\frac{1}{n-1}} \cdot \left(\Delta_n^{\frac{n}{2}}\right)^{\frac{1}{\frac{n(n-1)}{2}}}$$

$$\therefore \qquad < k^{\frac{1}{n-1}} \{\pi \sin^2 \xi_{rs}\}^{\frac{1}{\frac{n(n-1)}{2}}}.$$

Since the geometric mean is less than the arithmetic mean

$$\therefore \quad V < k^{\frac{1}{n-1}} \left\{\frac{\Sigma \sin^2 \xi_{rs}}{N}\right\}, \qquad N = \frac{n(n-1)}{2}.$$

$$i.e. \qquad < k^{\frac{1}{n-1}} \left\{1 - \frac{\Sigma \cos^2 \xi_{rs}}{N}\right\}.$$

Now $\Sigma\ \Delta_r \Delta_s \cos \xi_{rs} = \dfrac{\Delta^2_{n+1} - \overset{n}{\Sigma}\ \Delta_r^2}{2} = \Omega$ by equation (II).

$\therefore$ The smallest value of $\Sigma \cos^2 \xi_{rs}$ satisfying equation (II) is given by $\dfrac{\Omega^2}{\Sigma\ \Delta_r^2 \Delta_s^2}$.

$$\therefore \quad V \leqslant \left\{\frac{(\underline{|n-1})^n}{(\underline{|n})^{n-1}}\ \Delta_1 \Delta_2 \cdots \Delta_n\right\}^{\frac{1}{n-1}} \left\{1 - \frac{\Omega^2}{N \cdot \Sigma\ \Delta_r^2 \Delta_s^2}\right\}$$

and in 3 dimensions we have

$$V \leqslant \left\{\frac{2}{9} \Delta_1 \Delta_2 \Delta_3\right\}^{\frac{1}{2}} \cdot \left\{1 - \frac{\left(\frac{\Delta_1^2 + \Delta_2^2 + \Delta_3^2 - \Delta_4^2}{2}\right)^2}{3(\Delta_1^2 \Delta_2^2 + \Delta_1^2 \Delta_3^2 + \Delta_2^2 \Delta_3^2)}\right\}.$$

In case $\Delta_{n^2+1} = \Delta_1^2 + \Delta_2^2 + \Delta_n^2$, we can easily prove that the upper bound is actually

$$\left\{\frac{(\underline{|n-1})^n}{(\underline{|n})^{n-1}}\ \Delta_1 \cdots \Delta_n\right\}^{\frac{1}{n-1}}.$$

§ 6. *Uniqueness of the Orthogonal Tetrahedron.*

Now we will prove the uniqueness of the orthogonal tetrahedron in *3 dimensions* (satisfying the given condition of having for the areas of its faces the given numbers).

Let us call the angle between OP_2 and OP_3 as λ, OP_3 and OP_1 as μ and OP_1 and OP_2 as ν. Then the orthogonality condition will reduce to the following by easy calculation,

$$\frac{\tan\lambda}{\Delta_1} = \frac{\tan\mu}{\Delta_2} = \frac{\tan\nu}{\Delta_3} = p \qquad \text{(IV)}$$

and the equation (II) can be put as

$$\Delta_1\Delta_2\cos\xi_{12} + \cdots = \Omega = \frac{\Delta_4^2 - \Delta_1^2 - \Delta_2^2 - \Delta_3^2}{2}.$$

Now ξ_{12} is the angle between the normals to the plane OP_2P_3 and OP_1P_3. Therefore the actual dihedral angle will be $\pi - \xi_{12}$.

Let us call $\qquad \pi - \xi_{12} = C,\ \pi - \xi_{23} = A,\ \pi - \xi_{31} = B.$

Then the spherical Δ with sides λ, μ, ν will have angles A, B, C. Equation (II) becomes

$$\frac{\cos A}{\Delta_1} + \frac{\cos B}{\Delta_2} + \frac{\cos C}{\Delta_3} = -\frac{\Omega}{\Delta_1\Delta_2\Delta_3}.$$

Now $\qquad \cos A = \dfrac{\cos\lambda - \cos\mu\cos\nu}{\sin\mu\sin\nu}$

$\text{Tan}\,\lambda = p\,\Delta_1. \quad \therefore\ \cos\lambda = \dfrac{1}{\sqrt{1+p^2\Delta_1^2}},\ \sin\lambda = \dfrac{p\Delta_1}{\sqrt{1+p^2\Delta_1^2}}$, etc.

the radical having the same sign for the 3 angles by equation (IV). Substituting for cos A, etc., we have

$$\Sigma\,\frac{\dfrac{1}{\sqrt{1+p^2\Delta_1^2}} - \dfrac{1}{\sqrt{1+p^2\Delta_2^2}\,\sqrt{1+p^2\Delta_3^2}}}{\dfrac{p^2\Delta_2\Delta_3\Delta_1}{\sqrt{1+p^2\Delta_2^2}\cdot\sqrt{1+p^2\Delta_3^2}}} = \frac{-\Omega}{\Delta_1\Delta_2\Delta_3}$$

$$i.e., \qquad \Sigma\left\{\frac{(1+p^2\Delta_2^2)\,(1+p^2\Delta_3^2)}{1+p^2\Delta_1^2}\right\}^{\frac{1}{2}} = 3 - p^2\Omega$$

$$\therefore\ \{\Sigma\,(1+p^2\Delta_2^2)\,(1+p^2\Delta_3^2)\}^2 = (3-p^2\Omega)^2 \prod_{r=1}^{3}(1+p^2\Delta_r^2).$$

We will now call $\qquad \sum_1^3 \Delta_r^2 = A_1$

$$\sum_1^3 \Delta_r^2\,\Delta_s^2 = A_2$$

$$\Delta_1^2\,\Delta_2^2\,\Delta_3^2 = A_3.$$

$\therefore$ L.H.S. $= (3 + 2A_1p^2 + A_2p^4)^2$

R.H.S. $= (9 - 6p^2\Omega + p^4\Omega^2)\,(1 + p^2A_1 + p^4A_2 + p^6A_3).$

After simplification and putting $p^2 = t$ and removing the root $t = p^2 = 0$, we have R.H.S. − L.H.S. =

$$A_3\,\Omega^2\,t^4 + (A_2\Omega^2 - 6\Omega\,A_3 - A_2^2)\,t^3 + (A_1\,\Omega^2 - 6\,\Omega\,A_2 + 9A_3 - 4\,A_1\,A_2)\,t^2 + (\Omega^2 - 6A_1\,\Omega + 3A_2 - 4A_1^2 - A)\,t - (6\,\Omega + 3A_1)$$

$$= a_0\,t^4 + a_1\,t^3 + a_2\,t^2 + a^3\,t + a_4.$$

$$\Omega = \frac{\Delta_4^2 - \Delta_1^2 - \Delta_2^2 - \Delta_3^2}{2} = \frac{\Delta_4^2 - A_1}{2}.$$

$$\therefore\quad a_4 = -\{3\,(\Delta_2{}^4 - A_1) + 3A_1\} = -3\Delta_4{}^2$$

$$a_3 = \Omega^2 + 3A_2 - 4A_1^2 - 3A_1\,(\Delta_4{}^2 - A_1) = \Omega^2 - A_1^2 + 3\,(A_2 - A_1\,\Delta_4{}^2).$$

Now, $\Delta_1 \leqslant \Delta_2 \leqslant \Delta_3 \leqslant \Delta_4 < \Delta_1 + \Delta_2 + \Delta_3$.

$$\therefore\quad \Delta_4{}^2 \leqslant 3\,(\Delta_1{}^2 + \Delta_2{}^2 + \Delta_3{}^2)$$

Now $$\frac{\Delta_4^2 - \Delta_1^2 - \Delta_2^2 - \Delta_3^2}{2} \leqslant \Delta_1{}^2 + \Delta_2{}^2 + \Delta_3{}^2 = A_1.$$

In case $\Delta_4{}^2 \leqslant A_1$. Then $|\Omega| < A_1$

In case $\Delta_4{}^2 \geqslant A_1$. Then by above $|\Omega| \leqslant A_1$

$$\therefore\quad \Omega^2 - A_1{}^2 \leqslant 0$$

Since $\Delta_4 \geqslant \Delta_3 \geqslant \Delta_2 \geqslant \Delta_1$

$$A_2 \leqslant A_1.\ \Delta_4{}^2.$$

$$\therefore\quad a_3 \text{ is also } \leqslant 0$$

$$a_2 = A_1\,\Omega^2 + 9A_3 - 4\,A_1A_2 - 6A_2\,\Omega.$$

Case I.—Let $\Omega \leqslant 0$, *i.e.*, $\Delta_4{}^2 \leqslant \Delta_1{}^2 + \Delta_2{}^2 + \Delta_3{}^2$

Then $a_2 = A_1\,\Omega^2 + 9A_3 - 4A_1A_2 - 3A_2\,(A_1 - \Delta_4{}^2)$

$$= A_1\,(\Omega^2 - A_2) + 3\,(3A_3 - A_2\,\Delta_4{}^2).$$

Since $\Delta_4 \geqslant \Delta_3 \geqslant \Delta_2 \geqslant \Delta_1$, $3A_3 < A_2\,\Delta_4{}^2$

and $$4\,(\Omega^2 - A_2) = (\Delta_1{}^2 + \Delta_2{}^2 + \Delta_3{}^2 - \Delta_4{}^2)^2 - 4\sum_1^3 \Delta_2{}^2\,\Delta_3{}^2$$

$$= [\Delta_1{}^4 + \Delta_2{}^4 + \Delta_3{}^4 - \Delta_4{}^2\,(\Delta_1{}^2 + \Delta_2{}^2 + \Delta_3{}^2)] + \Delta_4{}^2\,(\Delta_4{}^2 - \Delta_1{}^2 - \Delta_2{}^2 - \Delta_3{}^2) - 2\sum_1^3 \Delta_2{}^2\,\Delta_3{}^2$$

Since $\Delta_4 \geqslant \Delta_3 \geqslant \Delta_2 \geqslant \Delta_1$ and since $\Omega \leqslant 0$, each of the expressions on the R.H.S. is negative.

$$\therefore\quad a_2 \leqslant 0.$$

Case II.—$\Omega > 0$

$$a_2 = A_1\left(\Omega - \frac{3A_2}{A_1}\right)^2 - \left\{4A_2 - \frac{9A_3}{A_1}\right\} - \frac{9A_2^2}{A_1^2}.$$

We notice that $3A_1 A_2 > 9A_3$. (Easily provable.)

$\therefore$ Since $\Omega > 0$

If a_2 is to be > 0.

Then Ω should be $> \dfrac{3A_2}{A_1} + \sqrt{\dfrac{9A_2^2}{A_1^2} + A_2 + \left(3A_2 - \dfrac{9A_3}{A_1}\right)}$

Consider $a_1 = A_2\,\Omega^2 - 6A_3\,\Omega - A_2^2$

$= A_2\left(\Omega - \dfrac{3A_3}{A_2}\right)^2 - A_2 - \dfrac{9A_3^2}{A_2}\Big)$

$= A_2\left\{\Omega - \dfrac{3A_3}{A_2} - \sqrt{A_2 + \dfrac{9A_3^2}{A_2^2}}\right\}\left\{\Omega - \dfrac{3A_3}{A_2} + \sqrt{A_2 + \dfrac{9A_3^2}{A_2^2}}\right\}$

Now $\dfrac{3A_2}{A_1} + \sqrt{\dfrac{9A_2^2}{A_1^2} + A_2 + \left(3A_2 - \dfrac{9A_3}{A_1}\right)}$

$> \dfrac{3A_2}{A_1} + \sqrt{A_2 + \dfrac{9A_2^2}{A_1^2}}.$

Since $\dfrac{A_2}{A_1} > \dfrac{3A_3}{A_2}$ and much more so $\dfrac{A_3}{A_2}$.

(easily provable)

$\therefore \quad \dfrac{3A_2}{A_1} + \sqrt{A_2 + \dfrac{9A_2^2}{A_1^2}} > \dfrac{3A_3}{A_2} + \sqrt{A_2 + \dfrac{9A_3^2}{A_2^2}}.$

$\therefore$ Whenever under Case II ($\Omega > 0$)

$$a_2 \geqslant 0$$

then $a_1 \geqslant 0$

a_0 being > 0. The coefficients a_0, a_1, a_2, a_3, a_4 will have the following signs Case I $+$? $-$ $-$ $-$. Whatever be the sign of a_1, by Descartes' rule the equation will have exactly one positive root.

Case II.—$a_2 > 0$. Then the coefficients a_0 a_1 a_2 a_3 a_4 will have the following signs $+$ $+$ $+$ $-$ $-$.

We therefore see that the equation has in this case also one and only one positive root.

We have therefore established that in all cases the equation will have one positive root only. Hence the uniqueness of the orthogonal tetrahedron having the maximum volume and the given numbers for the areas of its faces is proved.

The same method of investigation for proving the uniqueness or otherwise of the maximum orthogonal tetrahedron cannot be followed for the n-dimensional case.

THE VOLUME OF A TETRAHEDRON, THE AREAS OF THE FACES BEING GIVEN.

By Faqir Chand Auluck.

Received February 7, 1938.
(Communicated by Dr. S. Chowla.)

At the last Science Congress, Prof. A. Narasinga Rao raised the following question about a tetrahedron : " The areas of the four faces of a tetrahedron are $\alpha, \beta, \gamma, \delta$. Is the volume determinate ? If not, between what limits does it lie ?"

In this paper I prove that the volume is indeterminate but the volume has an upper bound. On the other hand, there is no lower bound: I indicate a method for finding the stationary values of the volume and prove that they are finite in number.

1. To Determine the Stationary Values of the Volume.

Let p be the perpendicular OD from O, a vertex, to the opposite face ABC whose area is δ where $\delta \geqslant \alpha, \beta$ and γ. The volume V of the tetrahedron is $\frac{1}{3} p\delta$.

If a, b, c are the sides of the Δ ABC

$$16\,\delta^2 = \Sigma\,(2b^2c^2 - a^4) \tag{1}$$

Through DO draw a plane perpendicular to the line BC. The lines of intersection of this plane with the planes ABC and BCD are perpendicular to BC.

Area of Δ BCD $= \frac{1}{2}a\sqrt{\frac{4\alpha^2}{a^2} - p^2} = \sqrt{\alpha^2 - \frac{a^2p^2}{4}}$

It follows that

$$\Sigma\sqrt{\alpha^2 - \frac{a^2p^2}{4}} = \delta \tag{2}$$

taking the necessary signs.

If $V \to \infty$, then $p \to \infty$

and in order that relation (2) may hold a, b, c should tend to limit zero, *i.e.*, $\delta \to 0$ which is not the case.

$$\text{Put } u^2 = \frac{\alpha^2 - \frac{a^2p^2}{4}}{\delta^2};\ v^2 = \frac{\beta^2 - \frac{b^2p^2}{4}}{\delta^2};\ w^2 = \frac{\gamma^2 - \frac{c^2p^2}{4}}{\delta^2} \tag{3}$$

$$(2) \text{ reduces to } u + v + w = 1, \tag{4}$$

where u, v, w may be positive or negative and (1) becomes

$$p^4\delta^2 = \Sigma\ [2\ (\beta^2 - v^2\delta^2)\ (\gamma^2 - w^2\delta^2) - (\alpha^2 - u^2\delta^2)^2] \tag{5}$$

or putting $\frac{\alpha}{\delta} = A$, $\frac{\beta}{\delta} = B$, $\frac{\gamma}{\delta} = C$

$$\frac{p^4}{\delta^2} = \Sigma\ [2(B^2 - v^2)\ (C^2 - w^2) - (A^2 - u^2)^2] \tag{6}$$

Therefore (6) has stationary values consistent with (4) if

$$u\ (B^2 + C^2 - A^2 - v^2 - w^2 + u^2) = v\ (C^2 + A^2 - B^2 - w^2 - u^2 + v^2)$$
$$= w\ (A^2 + B^2 - C^2 - u^2 - v^2 + w^2).$$

Therefore $\frac{1}{v} + \frac{1}{w} \propto (A^2 - u^2)$

or

$$\frac{A^2 - u^2}{u\ (1 - u)} = \frac{B^2 - v^2}{v\ (1 - v)} = \frac{C^2 - w^2}{w\ (1 - w)}\ .$$

and hence

$$\frac{A^2 - u^2}{A^2 - u} = \frac{B^2 - v^2}{B^2 - v} = \frac{C^2 - w^2}{C^2 - w} = \theta \tag{7}$$

where θ is to be determined.

Solving for u, v, w and substituting in (4) we get

$$2 - 3\theta = \Sigma \pm \sqrt{\theta^2 - 4A^2(\theta - 1)}$$

which on simplification becomes

$$[\{(2 - 3\theta)^2 - 3\theta^2 + 4(\theta - 1)\ (A^2 + B^2 + C^2)\}^2$$
$$- 4\Sigma\ \{\theta^2 - 4B^2(\theta - 1)\}\ \{\theta^2 - 4C^2(\theta - 1)\}]^2$$
$$= 64\ (2 - 3\theta)^2\ \Pi\ \{\theta^2 - 4A^2(\theta - 1)\}] \tag{8}$$

Coefficient of $\theta^8 = 0$.

There are at most 7 real values of θ. Hence (4) and (7) give only a finite number of sets of values of u, v, w and hence we can determine all the stationary values of V from (5).

*2. The Volume has an Upper Bound but no Lower Bound.**

From (5) we can get as many values of p as we like and therefore, in general, the areas of the faces do not fix the volume of the tetrahedron.

The maximum volume that the tetrahedron can have does not tend to infinity and is among the stationary values found above.

Let $b = \frac{c\beta}{\gamma}$.

* The method of proof is due to S. Chowla.

Consider the function

$$\phi(a, c, p) = \left\{\sqrt{\alpha^2 - \frac{a^2p^2}{4}} + \beta\sqrt{1 - \frac{c^2p^2}{4\gamma^2}} + \sqrt{\gamma^2 - \frac{c^2p^2}{4}} - \delta\right\}$$

$$\phi(a, c, 0) = \alpha + \beta + \gamma - \delta > 0$$

for otherwise the tetrahedron cannot be constructed.

$$\phi\left(a, c, \frac{2\gamma}{c}\right) = \sqrt{\alpha^2 - \frac{a^2\gamma^2}{c^2}} - \delta < 0$$

for $\alpha \leqslant \delta$.

Therefore $\phi(a, c, p) = 0$ for a value of p between 0 and $\frac{2\gamma}{c}$.

But we can take c as large as we like by diminishing a so that the area of the Δ ABC remains constant and therefore p can be made smaller than any quantity however small. Hence the volume has no lower bound.

TECHNIQUE OF THE PAINTING PROCESS IN THE TEMPLE OF VIJAYALAYA CHOLISVARAM IN THE PUDUKKOTTAI STATE.[1]

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Received March 28, 1938.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

Introduction.

While experimental investigations have been carried out by Chaptal,[2] Davy,[3] Berger,[4] Raehlmann,[5] Laurie,[6] Nöel Heaton[7] and Eibner[8] to reconstruct the methods of production of ancient mural paintings in the West, very little has been done in this direction for Indian paintings. With the exception of the paintings in the Brihadisvara temple at Tanjore,[9] in the cave temple at Sittannavasal,[10] and, to a limited extent, of Ajanta,[11] no other Indian painting has so far been investigated. Recently the author had an opportunity of studying the chemistry of the methods and materials used in the paintings* on the inner walls of the front hall of the ruined temple of Vijayalaya Cholisvaram, which is situated on a hillock in the village of Narttamalai (10° 31′ N. and 78° 45′ E.) in the Pudukkottai State in S. India. These paintings probably belong to the 14th–15th centuries A.D.†

Experimental Investigations.

In order to determine experimentally the painter's methods and materials, some fragments of painted stucco were collected from relatively unimportant places. They consisted of rough lime plaster, which had been

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* There are figures of Bhairava, Nataraja and Sakti (?) on the northern wall of the front hall of the temple. On the southern wall, the paintings have almost disappeared leaving only three heads, and a hand with finger nails in white.

† Dr. C. Minakshi drew my attention to a stone inscription in the temple which speaks of the destruction of the temple by rains and its subsequent renovation (*vide* S. R. Balasubrahmanyan and K. Venkataranga Raju, "Narttamalai and its temples—The Vijayalaya Cholisvaram temple in Mela Malai," *Journal of Oriental Research, Madras*, 1934, **8**, 208).

On palæographic evidence, this inscription belongs to the 12th century A.D. But there is no mention of the paintings in it, so that they should have been executed after the 12th century A.D. From a comparative study of the style of the paintings here with those of the Chola and the Nayak Paintings in the Brihadisvara temple at Tanjore (*vide* S. Paramasivan, "A Note on the dating of the frescoes in the Brihadisvara temple at Tanjore," *Journal of Oriental Research, Madras*, 1935, **9**, 363), it seems probable that these paintings, or at least most of them, belong to the 14th–15th centuries A.D.

laid on the wall, with a smooth coat of lime-wash thereon to receive the paint. The thickness of the painted stucco varies from about 3 mm. to 4 mm. In some places, the minimum thickness is about 2·3 mm. and the maximum about 12·7 mm. depending upon the inequality of the surface on which it had been laid.

In the production of paintings, there are four principal factors to be considered: (1) the *carrier* which supports the *ground*, (2) the *ground* on which the paintings are executed, (3) the *pigments* used in elaborating the designs, and (4) the *binding medium* by which the pigments are attached to the *ground*. Of these four factors, the last one is specially important. It determines the technique employed in the painting process, that is, whether it is one of *fresco*, *tempera* or any other. It also exerts a certain influence on the optical effects of the pigments, and gives a certain indication of the technique of the painter's art.[12]

1. The Carrier.

The inner walls of the front hall of the temple act as the *carriers*. The inner and the outer walls of this hall are constructed of large blocks of hornblende-gneiss, measuring roughly 2′ 1″ by 9″, with hollow space between. The hollow space has been filled with concrete composed of mortar and small pieces of brick. The inner walls have rough surfaces, which act as "tooth" so that the rough plaster or the first application of rough plaster adheres firmly to them.[13] In many places, the blocks of stone of which the walls are constructed have been displaced with the result that the *ground* and the paintings have fallen down.‡ The paintings are covered with white efflorescence caused by the presence of gypsum, sodium sulphate, magnesium sulphate, etc. These must be removed by washing with water before the paintings are made clear. The efflorescence can be traced to the *carrier*.§

‡ As a result of unequal expansion, the concrete mixture has displaced the blocks of stone of which the walls are constructed, thus disturbing the *ground* and weakening its hold on the wall. The damage which the *ground* and the paintings have suffered is not a little due to this.

§ While a hard, non-porous wall will eliminate all chance of salt efflorescence, the paintings here are not free from them. The reasons are not far to seek. While water on the surface of a fresco does no damage to it, a wet wall behind it ruins the paintings entirely. The moisture penetrates into the plaster ground and carries with it any salt that might be present in solution to the surface. There they crystallise forming white or coloured efflorescence upon the paintings. Moisture breeds moulds too, and is, on every account, disastrous to lime paintings on walls. The moisture should have crept from the ground between the inner and the outer walls and the concrete mixture, through the weak binding between the blocks of stone, carrying with it the salts in solution.

2. The Ground.

A series of experiments were conducted to study the nature of the *ground* that has been prepared to receive the paintings.

Nature of the Particles in the Plaster.—(i) The rough plaster was subjected to mechanical separation by carefully breaking it down under water and washing out the finer particles through a 70-mesh brass wire-cloth sieve and pestled with a rubber pestle until a clean residue was left on the sieve. The mesh retained particles whose diameters were greater than 0·2 mm. There was almost no particle of this size present in the plaster. The particles were next subjected to mechanical separation by the application of a principle enunciated in Stoke's Law, namely, that the limiting velocity of a particle falling in a fluid is proportional to the square of its diameter. The separation of the particles composing the stucco was effected by Robinson's method[14] and thus particles whose diameters were greater than 0·02 mm., but less than 0·2 mm. were separated from still finer particles. The former consisting mostly of sand was present to the extent of 60%, while the remaining 40% consisted of fine sand, lime and a little of clay.

(ii) A small fragment of the rough plaster was treated with dilute hydrochloric acid. The lime dissolved in the acid, leaving the particles of sand unaffected. The latter were almost of uniform size to the naked eye. Under the microscope, they looked sharp and angular,¶ without being rounded, and varied in size from 0·0014 mm. to 0·0042 mm. A few of them varied in size from 0·0070 mm. to 0·0643 mm.

Study of the Microsection.—With the help of a fine saw, the fragment of the painted plaster was cut across vertically through the different layers composing it. The freshly exposed edge was ground to a flat surface by rubbing it on a plate of ground glass. It was then carefully treated with dilute hydrochloric acid to remove the fine dust. Thus a section showing all the different layers of the painted stucco was prepared.

An examination under the microscope revealed two lines of cleavage at depths of 0·6 mm. and 1 mm. respectively below the top of the painted layer. They suggest two separate junctions due the presence of three distinct layers in the stucco. The first junction is between the layer of paint and the lime-wash, and the second, between the lime-wash and the rough plaster. Their respective thicknesses may be set down thus :

¶ These sharp and angular grains interlock with each other, hold more firmly and thus contribute better to the firmness of the plaster than would be the case with rounded grains which would slide on one another.

		mm.
Painted Stucco	..	3·3
Rough Plaster	..	2·3
Lime-wash	..	0·4
Paint Film	..	0·6

From the difficulty in effecting a separation between the rough plaster and the lime-wash, it is clear that the binding is very strong. Probably, the lime-wash was given while the rough plaster was still wet. The layer of paint can be easily separated from the lime-wash, and this shows that the binding here is not so strong as between the rough plaster and the lime-wash.

Analysis of the Plaster.—To determine how the rough plaster was prepared, its composition was ascertained. For this purpose, a few samples of stucco completely freed of the paint and the lime-wash was analysed. The results of analysis of representative specimens are as follows:

	Rough Plaster (per cent.)
Moisture	1·39
Carbon dioxide (CO_2)	20·95
Loss on ignition (excluding moisture and carbon dioxide)	4·29
Silica (SiO_2)	37·83
Iron and Alumina (Fe_2O_3 and Al_2O_3)	1·79
Lime (CaO)	31·73
Sulphuric anhydride (SO_3)	0·03
Magnesia	0·66
Undetermined (Mostly alkalis)	1·33
TOTAL ..	100·00

Thus the ground is composed of lime plaster with lime and sand as the principal components. The causes leading to their consolidation are very well known.[15]

From the results of analysis, it is clear that—

(i) A pure rich lime was used having no hydraulic properties. The proportion of clay, as is evident from the amount of iron and alumina, is very small. If it were hydraulic, a much larger percentage of clay would have been present.

(ii) Gypsum in plaster prevents its setting and gives rise to efflorescense. Thus it is an element of weakness in the *ground* so that the quality of lime for painting is determined by its gypsum content. But the proportion of it is very low as shown by the amount of sulphuric anhydride.

(iii) Pure rich lime without the admixture of sand or other 'inert' material is not satisfactory for plaster. It becomes friable on carbonation and lacks setting power. The function of the inert material is to provide the necessary space for expansion between the particles of lime. The percentage of silica is too large to be taken merely as an impurity, but should have been purposely added as sand to serve as an inert material.

The preparation of the lime for the *ground* is too well known to be discussed here.[16]

Inert Materials in the Plaster.—The results of chemical analysis do not reveal the presence of any other inert material except sand. If the artist had added marble dust‖ or powdered shell or limestone—the original material from which the caustic lime was prepared—as an inert material, the problem would be different. Since these substances have the same chemical composition and give the same chemical reactions, they could not have been identified in the course of chemical analysis, and the following further experiments were necessary to decide their presence :—

(i) A microscopic slide was prepared from a fragment of plaster from the painted stucco reduced to fine powder, and this was examined under the microscope. Similar parallel experiments were made with fragments of modern plaster (without marble dust) to which a known proportion of marble dust was added. While the former yielded uniformly fine particles without any recognisable crystalline forms, the latter showed crystalline particles characteristic of marble.

Under polarised light, the fragments of crystalline marble showed themselves bright on a dark ground. Under the same conditions, the fragments of plaster from the temple remained entirely dark, no crystals other than those of silica being revealed. The results were identical in all the specimens of plaster collected.

It may be argued that the marble dust, originally present, might have interacted with the lime in the plaster, and become converted into non-crystalline carbonate. This theory is untenable because Davy[17] has identified marble dust in the ancient stuccoes in the ruins of the baths of Titus,

‖ In Italy, the ancient practice was to add marble dust as an inert material to the lime in the preparation of plaster.

Livia, etc., which are more than 1,000 years old. While marble dust has not changed in the classical stuccoes, there is no reason why it should have changed in the plaster of Vijayalaya Cholisvaram temple, which date from much later times.

(ii) If limestone or shell had been used as an inert material, it would have been very difficult to powder it to such a degree of uniform fineness that fragments of it could not be isolated and recognised by microscopic examination. The following experiments were conducted in this connection :—

(*a*) The surface of the plaster was etched with dilute hydrochloric acid on a microscopic slide and the process of disintegration observed under the microscope. Even under careful observation, larger particles were not seen.

(*b*) Taking a small fragment of the plaster, the lime was completely dissolved in dilute hydrochloric acid and the insoluble residue was examined under the microscope. In all cases, the residue consisted of small fragments of silica with iron oxide as impurity, and the latter was always in anhydrous condition as red ferric oxide indicating that the lime containing them had been burnt. In the absence of any fragments of hydrated yellow oxide, it is clear that no unburnt shell or limestone had been used.

(*c*) A fragment of the plaster was carefully reduced to powder so as to separate the grains without breaking them up. A study of the density of the powdered plaster by means of a diffusion column[18] showed that the specific gravity of all the carbonated lime particles was almost the same and that there were no particles which corresponded to the density of limestone (2·72) or of shell (2·55). It is thus shown that no unburnt shell or limestone had been used in the plaster as an inert material.

Technique of Laying the Ground.—The rough plaster suffers a loss of weight on ignition to the extent of 4·29%, which shows that some organic matter is present in it either as a binding medium or as an impurity. Thus the next problem is to determine whether the technique employed in laying the *groumd* in one of fresco or tempera. The following experiment was conducted to settle this point :—

A fragment of the plaster was treated with dilute hydrochloric acid. It completely disintegrated under the action of the acid with evolution of carbon dioxide, and the solution gave tests for calcium, thus showing that the technique employed in laying the ground was one of fresco. Had it been tempera, the plaster would have remained as a flake without disintegrating under the action of the acid.

Method of Laying the Ground.—The experimental results indicate that the artists applied the first coat of rough plaster to a thickness of about

2·3 mm. In a few places the thickness varied up to 12·7 mm. according to the inequalities of the surface of the wall. The plaster then received the lime-wash $ to a thickness of about 0·4 mm. From the strong binding between the rough plaster and the lime-wash it is evident that the latter was applied while the former was still wet.

3. The Pigments.

Six colours were recognisable in the fragments of painted stuccoes that were collected, namely, white, black, yellow, red, green and bluish green. Their identification was as follows :—

White.—This dissolved in dilute hydrochloric acid with evolution of carbon dioxide and the solution gave tests for calcium. The colour thus consists of calcium carbonate originally employed as the hydrate of lime.

Black.—It lost the colour on ignition with evolution of carbon dioxide and suffered loss in weight. It also left a colourless residue, which was soluble in water and acids. It did not give any tests for calcium phosphate, nor did it give an extract either with ether or carbon disulphide. All these experiments clearly showed that it was not bone-black or lamp-black, but only wood charcoal.

Yellow.—Its appearance under the microscope was very heterogeneous with particles of various colours and of different optical properties, yellow and brown predominating along side of colourless and light coloured particles.[19a] On ignition, the yellow was converted into a pigment similar to Venetian red. This pigment was also characterised by the presence of iron, which was detected as Prussian blue after evaporating it several times with strong hydrochloric acid and testing with potassium ferrocyanide. These are characteristic of ochres.

Red.—Its appearance under the microscope differed little from that of the ochres generally. There was only one kind of coloured particles, and not, as in the case of yellow ochres, particles of various tints. There were also colourless particles, which were doubly refractive. These are all characteristic of red ochre,[19b] the iron in which was detected as Prussian blue as in the case of yellow ochres.

Green.—Under the microscope, it gave the impression of a product with a heterogeneous composition resembling a mixture containing an

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$ The untreated surface of the wall is not ideal for painting. It cannot always be made perfectly smooth and even, and different parts of the grain take the paint differently and thereby produce different optical effects. Thus the lime-wash serves a double purpose; first, to even out the wall surfaces to which they are applied, and secondly to provide a uniform ground underneath the painting.

ochre with some blue pigment. Though the blue resembled cobalt blue, it gave negative tests for cobalt. Further, the blue was doubly refractive, which is not the case with cobalt blue. On igniting it several times with strong sulphuric acid, the iron in it, which is quite characteristic, was confirmed as Prussian blue.[19c]

Further tests were applied to confirm the result. On adding dilute hydrochloric acid to the green on a microscopic slide, it did not dissolve. On allowing it to dry and adding a drop of dilute solution of sodium hydroxide, the colour was not affected. On warming it with a drop of concentrated hydrochloric acid, it was not affected or dissolved except that there was slight effervescence.[20a] All these reactions are characteristic of terre verte.

Bluish Green.—Under the microscope, particles of blue and green were distinctly visible. The green gave tests similar to the ones indicated under terre verte. The blue particles were not birefringent. They were decolourised by dilute hydrochloric acid, but no green-to-brown residue was obtained with as copper compounds. The experiments showed that the blue particles consist of ultramarine.[20b] The bluish green is thus a mixture of terre verte and ultramarine.

4. *The Binding Medium.*

As explained already, the binding medium determines the nature of the painting process, that is, whether it is one of fresco, tempera, oil or encaustic. In the case of tempera, the problem of identifying the binding medium is difficult and complex. Here the binding media are not well-defined substances, but are accidental mixtures such as nature furnishes in the form of gum, resin, linseed or poppy seed oil, albumin, etc. The problem of their identification is complicated by three facts, namely, (i) the amount necessary to fix a pigment to a surface is very small ; (ii) even if the binding medium remains *in situ*, it changes its character in course of time through the chemical actions of moisture and atmospheric oxygen ; (iii) since the chemist cannot be allowed to destroy large surfaces of paintings, he can get only small fragments of the painted layer from which to extract the binding medium. For these reasons, it becomes exceedingly difficult to decide definitely what they were originally composed of. While the identification of the particular organic medium is difficult, its presence or absence is not difficult to settle, even though small amounts of it are available.

The following experiments were carried out to determine the nature of the binding medium :—

(i) The paint layer was brushed over with a wet sponge and rubbed with the fingers. A small fragment of it was soaked in water and the water boiled for 15 minutes. In all these cases, there was no damage or injury to the painting. It was noted that the pigment had not penetrated into the plaster.

(ii) A fragment of the paint layer was treated with pure ether and other solvents like chloroform and carbon disulphide. With these solvents no vehicle was extracted.

(iii) A fragment of the paint film was treated with dilute hydrochloric acid. It did not disintegrate, but there was considerable effervescence with evolution of carbon dioxide, and the fragment remained as a flake. Had tempera process been employed, there would have been no effervescence and evolution of carbon dioxide, but the paint film would have remained as a flake.

These experiments showed that the medium employed was both tempera and lime, in fact, a combination of both. Further experiments were necessary to elucidate this point.

A portion of the paint film was carefully separated from the underlying lime-wash and analysed, the results of chemical analysis being as follows :—

	Red paint film (per cent.)
Moisture	1·71
Carbon dioxide	11·67
Loss on ignition (excluding moisture and carbon dioxide) ..	11·86
Silica (SiO_2)	38·85
Alumina (Al_2O_3)	0·73
Iron (Fe_2O_3)	6·90
Lime (CaO)	25·09
Sulphuric anhydride (SO_3)	0·27
Magnesia (MgO)	1·68
Undetermined (Mostly alkalis)	1·24
	100·00

It is clear from the results of analysis that the percentage of iron is higher here than in the rough plaster. This is due to the fact that the fragment chosen for analysis was a red paint, for which red ochre had been used.

The interesting point to be considered is the loss of weight on ignition, to the extent of 11·86%, which is very much higher than with the rough plaster. This can be explained only on the assumption that an organic substance has been purposely or accidentally added as the binding medium to fix the pigments to the plaster. At the same time, the presence of lime in the results of analysis shows that it was purposely added to the pigment as a binding medium.

The following experiments were conducted to find out the nature of the organic medium :—

(i) A sample of the paint layer was subjected to Lessaigne's test for nitrogen, but it failed to give the Prussian blue colour, thereby showing the absence of nitrogenous substance in the binding medium.

(ii) The absence of nitrogenous substance in the binding medium is proved further by the absence of any stain characteristic of glue, albumin or casein with either acid green (dissolved in water to which a little hydrochloric acid had been added) or iodoeosin (dissolved as the ammonium salt).[21a]

(iii) A drop of freshly prepared dilute solution of methyl violet placed on a fragment of the paint film for over 15 minutes, yielded violet colouration.[21b] This indicated the presence of a drying oil. Under these conditions, neither resin nor glue nor any nitrogenous substance will be dyed by methyl violet. A freshly prepared dilute solution of methylene blue gave the same violet stain characteristic of drying oil.[21c]

Thus the presence of an organic binding medium in the paint film is due to some drying oil. It is not quite clear whether the oil was added accidentally or purposely to the original material, thus imparting the additional characteristic of tempera technique to simple painting in lime medium.

In conclusion, the author desires to express his thanks to the Pudukkottai Darbar for providing him with all facilities to study the paintings *in situ* and to Sir Alexander Tottenham, C.I.E., Administrator of the Pudukkottai State, and to Dr. F. H. Gravely, Superintendent of the Government Museum, Madras, for their encouragement and kind interest in the work.

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QUESTION OF INVARIANCE IN THE NEUTRINO THEORY OF LIGHT.

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§ 1. *Introduction.*

The neutrino theory of light, initiated by Jordan, has been developed in a series of papers by Jordan, Kronig, Born, Nagendra Nath, Pryce and others.[1] The essential point of the theory is the setting up of a relation between the neutrino operators and the photon operators such that while the former satisfy the commutation laws pertaining to the Fermi-Dirac statistics the latter satisfy those of the Einstein-Bose statistics. I have examined in this paper the question of Lorentz-invariance of this fundamental relation connecting the two sets of operators, and, by considering rotations of the frame of reference, shown that the relation itself is not invariant.

§ 2. *The Relation between the Operators.*

I shall use, here, the form of Jordan's relation as given by Nagendra Nath[2] wherein he takes the spin also into consideration.

$$b_{k,\rho} = \frac{-1}{\sqrt{2k}} \sum_{l=-\infty}^{+\infty} \sum_{i} a_{l,i}\, \gamma_{k-l,i} \qquad (1, a)$$

$$b_{k,\lambda} = \frac{-1}{\sqrt{2k}} \sum_{l=-\infty}^{+\infty} \sum_{i,j}{}' a_{l,i}\, \gamma_{k-l,j} \qquad (1, b)$$

or, using the relation $\gamma_{-k} = a_k^{\dagger}$, and the commutation laws for a's and γ's, in the form

$$b_{k,\rho} = \frac{1}{\sqrt{2k}} \sum_{l=-\infty}^{+\infty} \sum_{i} a_{l,i}^{\dagger}\, a_{l+k,i} \qquad (2, a)$$

$$b_{k,\lambda} = \frac{1}{\sqrt{2k}} \sum_{l=-\infty}^{+\infty} \sum_{i,j}{}' a_{l,i}^{\dagger}\, a_{l+k,j} \qquad (2, b)$$

The indices i and j each take two values corresponding to the two spin states of the neutrino denoted by ρ and λ. By the aid of a simple formalism

[1] For a complete bibliography see the report by Kronig in the *Annales de l' Institut Henri Poincare*, **6**.

[2] *Proc. Ind. Acad. Sci.*, (A), **3** (1936), p. 452, equation (16).

we can get rid of the rather unsymmetrical nature of (2*a*) and (2*b*) where we have a summation over i only in the first, and a summation over i and j $(i \neq j)$ in the second. Introducing the unit matrix

$$\delta = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

and one of the Pauli-matrices σ_x (after removing the suffix x) as

$$\sigma = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

it can be seen easily that (2, *a*) — (2, *b*) are equivalent to the forms

$$b_{k,\rho} = \frac{1}{\sqrt{2k}} \sum_{l=-\infty}^{+\infty} \sum_{\mu,\nu} a_{l,\mu}{}^{\dagger}\, \delta^{\mu\nu}\, a_{l+k,\nu} \qquad (3,\ a)$$

$$b_{k,\lambda} = \frac{1}{\sqrt{2k}} \sum_{l=-\infty}^{+\infty} \sum_{\mu,\nu} a_{l,\mu}{}^{\dagger}\, \sigma^{\mu\nu}\, a_{l+k,\nu} \qquad (3,\ b)$$

where the Greek indices μ, ν take values 1 and 2.

§ 3. *Transforms of the Operators.*

We shall now examine how the operators a, $a^{\dagger}$ and b are transformed by a rotation of the frame of reference through an angle θ. Since the a's are spinor magnitudes the transformation matrix for them is given by[3]

$$T = e^{-\frac{1}{2}i\theta s}\ ; \quad T^{\dagger} = e^{\frac{1}{2}i\theta s}, \qquad (4)$$

where s is the spin-matrix

$$s = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \qquad (5)$$

and denoting the transformed quantities by placing a bar over them, we have

$$\left.\begin{aligned} \bar{a}_{l,\mu} &= \sum_{\nu=1}^{2} T_{\nu\mu}\, a_{l\nu} \\ \bar{a}_{l,\mu}{}^{\dagger} &= \sum_{\nu=1}^{2} a_{l,\nu}{}^{\dagger}\, T^{\dagger}_{\nu\mu} \end{aligned}\right\} \qquad (6)$$

The b-operators undergo the ordinary transformation

$$\left.\begin{aligned} \bar{b}_{k,\rho} &= \cos\theta \cdot b_{k\rho} + \sin\theta \cdot b_{k\lambda} \\ \bar{b}_{k,\lambda} &= -\sin\theta \cdot b_{k,\rho} + \cos\theta \cdot b_{k,\lambda} \end{aligned}\right\} \qquad (7)$$

§ 4. *Non-invariance of the Fundamental Relation.*

If the relations (3, *a*) — (3, *b*) should be invariant for rotations, they must remain true when a's and b's are replaced by $\bar{a}$'s and $\bar{b}$'s as given by

[3] See Frenkel: *Wave Mechanics* (Advanced Theory), 1934, pp. 346-62.

(6) and (7). Hence we must have (introducing the necessary dummy indices)

$$\cos\theta\cdot b_{k\rho} + \sin\theta\cdot b_{k,\lambda} = \frac{1}{\sqrt{2k}}\sum_{l=-\infty}^{+\infty}\sum_{\mu,\nu,\tau,\pi} a_{l,\nu}^{\dagger}\, T_{\nu\tau}^{\dagger}\, \delta_{\tau\pi}\, T_{\pi\mu}\, a_{l+k,\mu} \qquad (8,\ a)$$

$$-\sin\theta\cdot b_{k\rho} + \cos\theta\cdot b_{k\lambda} = \frac{1}{\sqrt{2k}}\sum_{l=-\infty}^{+\infty}\sum_{\mu,\nu,\tau\,\pi} a_{l,\nu}^{\dagger}\, T_{\nu\tau}^{\dagger}\, \sigma_{\tau\pi}\, T_{\mu\,\pi}\, a_{l+k,\mu} \qquad (8,\ b)$$

Summing up for the indices τ and π on the right-hand sides, we have them reducing to

$$\left.\begin{aligned}&\frac{1}{\sqrt{2k}}\sum_{l=-\infty}^{+\infty}\sum_{\mu,\nu} a_{l,\nu}^{\dagger}\,(T_{\nu 1}^{\dagger}\, T_{1\mu} + T_{\nu 2}^{\dagger}\, T_{2\mu})\, a_{l+k,\mu}\\ &\frac{1}{\sqrt{2k}}\sum_{l=-\infty}^{+\infty}\sum_{\mu,\nu} a_{l,\nu}^{\dagger}\,(T_{\nu 2}^{\dagger}\, T_{1\mu} + T_{\nu 1}^{\dagger}\, T_{2\mu})\, a_{l+k,\mu}\end{aligned}\right\} \qquad (9)$$

In the left-hand sides of (8, *a*) — (8, *b*) we can replace $b_{k\rho}$ and $b_{k\lambda}$ by means of (3, *a*) — (3, *b*) and they should then be identically the same as (9). This ought to give us the relations

$$\left.\begin{aligned}\cos\theta\cdot\delta^{\nu\mu} + \sin\theta\cdot\sigma^{\nu\mu} &= T_{\nu 1}^{\dagger}\, T_{1\mu} + T_{\nu 2}^{\dagger}\, T_{2\mu} && (10,\ a)\\ -\sin\theta\cdot\delta^{\nu\mu} + \cos\theta\cdot\sigma^{\nu\mu} &= T_{\nu,2}^{\dagger}\, T_{1\mu} + T_{\nu 1}^{\dagger}\, T_{2\mu} && (10,\ b)\end{aligned}\right\}$$

Equating the sides of (10, *a*) — (10, *b*) for the indices $\nu\mu = 11,\ 12,\ 21,\ 22$ and using (4) and (5) we see that these lead to the relations

$$\sin\theta = 0, \quad \cos\theta = 1, \quad \cos\theta = e^{i\theta} = e^{-i\theta}$$

which are not true for any value of θ (except $\theta = 0$). Thus the falsity of (10) establishes the non-invariance of the relation connecting the a- and b-operators.

REACTIVITY OF THE DOUBLE BOND IN COUMARINS AND RELATED α : β-UNSATURATED CARBONYL COMPOUNDS.

Part V. Action of Mercuric Acetate on Cinnamic Acid and Its Derivatives.

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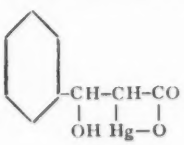
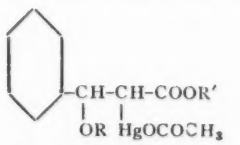
The addition of mercury salts to the double bond present in unsaturated acids was first studied by Biilmann[1] in aqueous solution and he came to the conclusion that high reactivity is associated with the *cis* structure and that *trans*-compounds do not react. He noticed that allocinnamic acid reacted readily with mercuric acetate to form compound (I) whereas ordinary cinnamic acid did not and hence deduced that the latter had the *trans* formula. Schoeller *et al*[2] employed alcoholic solution of esters of cinnamic acid and mercuric acetate and obtained products of the type (II). On saponifying the ester with alkali and subsequently adding acid, they obtained the internal anhydride of α-hydroxy-mercuri-β-alkoxy-β-phenyl-propionic acid (III). Sandborn and Marvel[3] used *l*-methyl cinnamate and were able to prove the formation of diastereoisomers. Wright[4] compared the reactivity of *cis* and *trans* methyl cinnamates and found that the former reacted much more rapidly than the latter and he was also able to collect useful evidence regarding the mechanism of the addition.

Schrauth and Geller[5] and Matejka[6] employed boiling alcoholic solutions of cinnamic acid and mercuric acetate and isolated compound (III). Quite

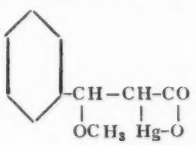


(I)



where R and R′ represent alkyl groups of the alcohol and ester respy.

(II)



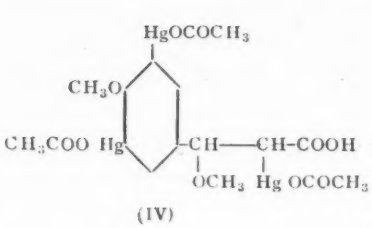
(III)

recently after the work described in the present paper had been completed, Loon and Carter[7] recorded some interesting observations on the effect of impurity in the acid and the time of reaction on the nature of the product.

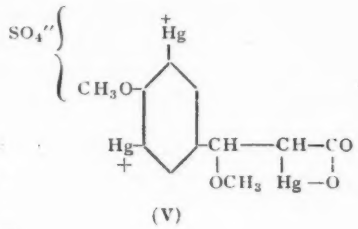
In the previous papers of this series,[8] it was shown that mercuric acetate can, besides adding to the double bond, mercurate the benzene nucleus also. The carboxylic acid form (IV) was frequently met with and the methoxy-dihydro-compounds produced by the action of hydrogen sulphide were found to be rather unstable. With a view to get more information on these aspects, the action of mercuric acetate on cinnamic, *p*-methoxy-cinnamic and *ortho*- and *meta*-nitrocinnamic acids has now been investigated in detail.

On mixing cold methyl alcoholic solutions of cinnamic acid and mercuric acetate, the mercury salt of cinnamic acid immediately separated out as a mass of colourless needles. These slowly dissolved even at the temperature of the room and compound (III) was formed as big rectangular prisms. The change was much quicker at the boiling point. Using very pure cinnamic acid we noticed no change in the chemical composition or properties on allowing the product to stay in the mother liquor for over a week. But even very small quantities of impurities produced definite changes in the solubility of the product though they were not so large as observed by Loon and Carter.

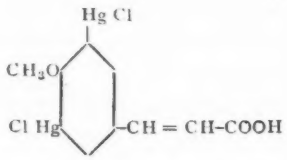
With equimolecular proportions of *p*-methoxycinnamic acid and mercuric acetate the mercury salt was immediately produced but it underwent very rapid conversion into the addition product. Even this could not be obtained pure since at the same time mercuration also took place to some extent. Therefore using excess of mercuric acetate the final product of addition and mercuration (IV), α : 3 : 5-triacetoxy-mercuri-β : 4-dimethoxy-dihydrocinnamic acid was obtained. Analytical results agree with the carboxylic formula. The positions of the acetoxy-mercuri-groups are assumed following the usual orienting influence of the methoxyl group. On adding dilute sulphuric acid to a solution of the substance in sodium hydroxide, sulphatomercuri compound (V) was formed whereas with dilute hydrochloric acid it formed 3 : 5-dichloro-mercuri-4-methoxy-cinnamic acid (VI) in which the addenda had been removed. These derivatives were useful in confirming the constitution of the mercuration product. The use of hydrochloric acid easily enabled a distinction between nuclear mercuration and addition at the double bond to be made since it invariably removed the addenda whereas sulphuric acid had no such influence.



(IV)



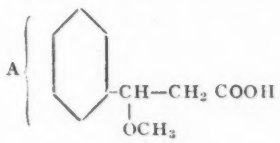
(V)



(VI)

m-Nitrocinnamic acid forms the mercuric salt in the cold immediately. This is quite stable and undergoes no change on long standing, whereas on heating, it slowly dissolves and forms the anhydride corresponding to (III). There is no mercuration. *o*-Nitrocinnamic acid does not react in the cold probably due to its low solubility in alcohol and the consequent high dilution of the solution, and on heating forms a similar addition product. No nuclear substitution could be expected since to the already inactive cinnamic acid the deactivating influence of the nitro group is added.

On treatment with hydrogen sulphide in alkaline solutions the methoxy-mercurials yielded the corresponding β-methoxydihydrocinnamic acids (VII), all the acetoxy-mercuri groups having been replaced by hydrogen atoms. These compounds were stable and were unaffected by prolonged treatment with dilute acid and alkali in the cold.



A—stands for H, OCH_3 or NO_2 group in the benzene nucleus.

(VII)

Experimental.

Para-methoxy- and *ortho*- and *meta*-nitrocinnamic acids were prepared from methoxy- and nitrobenzaldehydes by condensation with malonic acid using pyridine as catalyst.[9]

Action of mercuric acetate.

1. On cinnamic acid. Mercuric cinnamate.—The acid (2 g.) was dissolved in methyl alcohol (20 c.c.) and treated with a solution of mercuric acetate (4 g.) in methyl alcohol (50 c.c.) to which a few drops of acetic acid had been added. A bulky precipitate consisting of colourless fine needles was produced immediately. It was filtered and washed with small quantities of methyl alcohol containing a little acetic acid. It then melted at 194° with sintering at about 160°. (Found: Hg, 41·2; C, 43·1; $C_{18}H_{14}O_4Hg$ required Hg, 40·6; C, 43·7%.) When treated with aqueous sodium hydroxide it underwent decomposition to produce mercuric oxide and on adding dilute sulphuric acid to the alkaline mixture pure cinnamic acid could be isolated.

Anhydride of α-hydroxymercuri-β-methoxydihydrocinnamic acid (III).—When the mercuric salt was not filtered off and was allowed to stay in the mother liquor it underwent very slow conversion at 0° C. but at the temperature of the room (28° C.) it went into the solution again rather rapidly. If the volume of alcohol was sufficient a clear solution was obtained in the course of two hours and subsequently the more sparingly soluble compound (III), was deposited as colourless long rectangular rods. Even though with the volumes of alcohol mentioned in the previous experiment, no clear solution could be produced, the conversion was satisfactory and the anhydride was obtained pure in the course of 24 hours. After filtering and washing with methyl alcohol containing a little acetic acid the product melted at 212° with decomposition. (Found: Hg, 53·0; C, 31·3; $C_{10}H_{10}O_3Hg$ required Hg, 53·0; C, 31·7%.) It was easily soluble in chloroform and could be got into solution in aqueous potassium bromide by repeated treatment. It dissolved in aqueous sodium hydroxide without producing any trace of mercuric oxide and on acidifying the solution with dilute sulphuric acid it was reprecipitated. When aqueous hydrochloric acid was used instead, mercury was eliminated and cinnamic acid was liberated.

Compound (III) could be obtained more readily by heating the solutions as follows: cinnamic acid (4 g.) was dissolved in hot methyl alcohol (16 c.c.) and mixed with a similar solution of mercuric acetate (8 g.) in methyl alcohol (50 c.c.). A bulky precipitate of mercuric cinnamate was formed immediately. It however went into solution in the course of 10 minutes when the mixture was heated under reflux on a water-bath and the anhydride began to separate pure after another 10 minutes. The heating was stopped after half an hour, the mixture allowed to stand overnight and the product filtered and washed with methyl alcohol. The yield was about 9 g. and the

substance was identical in all respects with the sample obtained in the cold.

In one experiment the mixture was allowed to stand for a week and the solid product was isolated. It had undergone no change in its composition or properties. When a sample of cinnamic acid which was slightly coloured was employed and the mixture allowed to stand for seven days the composition was practically the same (Found : Hg, 52·9%) and its solubility in potassium bromide was also practically unchanged, but it did not dissolve completely in chloroform and it left behind a small insoluble residue.

With a view to examine the possibility of mercuration, cinnamic acid was boiled in methyl alcoholic solution with 4 molecular proportions of mercuric acetate for 40 hours. However the same anhydride (III) was obtained and there was no mercuration of the benzene nucleus.

β-Methoxydihydrocinnamic acid.—The mercury compound (2 g.) was dissolved in normal sodium hydroxide solution (20 c.c.) and hydrogen sulphide passed into it till all the mercury was precipitated as the sulphide ($\frac{1}{2}$ hour). After allowing the mixture to stand overnight the sulphide was filtered off and the clear filtrate acidified with dilute sulphuric acid. The solid that separated out in a crystalline form was recrystallised from hot water. It was obtained as colourless prisms melting at 97–8°. (Found : C, 66·3 ; H, 6·5 ; $C_{10}H_{12}O_3$ required C, 66·7 ; H, 6·7%.) The methoxy acid was readily soluble in all solvents and was unaffected in the presence of dilute acids and alkalies for several days.

2. *On para-methoxy-cinnamic acid.*—When equi-molecular proportions of the methoxycinnamic acid and mercuric acetate were mixed together in methyl-alcoholic solution in the cold the mercuric salt was immediately formed. But it underwent change so rapidly into the addition product that it could not be obtained pure. It decomposed at 161° and reacted with aqueous sodium hydroxide to produce mercuric oxide, but on further adding sulphuric acid the methoxycinnamic acid that was recovered was contaminated with a little combined mercury. In the course of 15 minutes the mercuric salt underwent complete transformation into a new product which decomposed at 204°. When filtered and washed with alcohol it dissolved in aqueous alkali to give a clear solution and most of the mercury was removed by adding hydrochloric acid. The methoxy acid that was obtained contained some mercury due to nuclear mercuration. The solid product was therefore mostly the addition compound with a portion that had further undergone mercuration in the benzene nucleus.

α : 3 : 5-*Triacetoxymercuri-β* : 4-*dimethoxy-dihydrocinnamic acid* (*IV*).—This was obtained by heating the acid with 4 molecular proportions of mercuric acetate as follows : the methoxy acid (5 g.) was dissolved in methyl alcohol (50 c.c.) and mixed with a solution of mercuric acetate (30 g.) in methyl alcohol (150 c.c.). No solid separated out in the cold as before. The mixture was heated under reflux for about 20 hours. Even then no solid was formed. It was only on adding more methyl alcohol to the solution after cooling that a crystalline looking solid was obtained. After the addition of sufficient amount of alcohol the product was filtered and washed with alcohol. It was then found to be very sparingly soluble in all organic solvents and to decompose at 181° (Found : Hg, 61·6 ; C, 20·7 ; $C_{17}H_{20}O_{10}Hg_3$ required Hg, 61·1 ; C, 20·7%.) It readily dissolved in aqueous sodium hydroxide to form a clear solution which deposited a colourless solid on adding dilute sulphuric acid. After filtering and washing repeatedly with water it was found to decompose at 223° and to correspond to formula (V). (Found : Hg, 66·2 ; $C_{11}H_{10}O_8Hg_3S$ required Hg, 66·6%.) If, on the other hand, the alkaline solution was acidified with dilute hydrochloric acid a different compound was obtained decomposing at 204°. This corresponded with 3 : 5-dichloro-mercuri-4-methoxy-cinnamic acid, the addenda having been removed by the acid. (Found : Hg, 62·4 ; $C_{10}H_8O_3Hg_2Cl_2$ required Hg, 61·9%.)

β : 4-*dimethoxydihydrocinnamic acid.*—By passing hydrogen sulphide into an alkaline solution of the above triacetoxy-mercuri-compound all the mercury was precipitated as the sulphide and filtered. On adding dilute hydrochloric acid, the dimethoxy-dihydrocinnamic acid was obtained as a crystalline solid which on recrystallisation from hot water appeared as colourless elongated needles melting at 144–45°. (Found : C, 62·6 ; H, 6·4 ; $C_{11}H_{14}O_4$ required C, 62·9 ; H, 6·7%.) The compound was quite stable in the presence of aqueous alkali and dilute hydrochloric acid.

3. On meta-nitrocinnamic acid. The mercuric salt.—On mixing methyl alcoholic solutions of the acid and mercuric acetate in the cold a bulky white precipitate was formed immediately. It was very sparingly soluble in the solvent and did not undergo any change over long periods. A sample of the salt collected after allowing the mixture to stand for 4 hours decomposed at 189°. It readily gave mercuric oxide on treatment with aqueous sodium hydroxide and the pure cinnamic acid was recovered on further addition of dilute sulphuric acid. (Found : Hg, 34·7 ; $C_{18}H_{12}O_8HgN_2$ required Hg, 34·3%.)

Anhydride of α-hydroxymercuri-β-methoxy-3-nitrodihydrocinnamic acid (corresponding to III).—If the alcoholic solutions of the acid and mercuric acetate were heated under reflux after mixing, the precipitated mercury salt redissolved and in the course of half an hour a fresh compound began to separate. The product was collected after heating for 10 hours and washed with methyl alcohol. It was found advisable to discard the first precipitate formed during the first half an hour as it was rather impure. The pure compound decomposed at 214°. (Found : Hg, 47·8 ; $C_{10}H_9O_5HgN$ required Hg, 47·4%.) It dissolved in alkali to form a clear solution and was reprecipitated on adding dilute sulphuric acid. With dilute hydrochloric acid the addenda were removed and *meta*-nitro cinnamic acid was obtained.

The same addition product was obtained on boiling the nitrocinnamic acid with a large excess of mercuric acetate for over 40 hours. No mercuration of the benzene ring could be noticed.

β-Methoxy-3-nitrodihydrocinnamic acid was obtained in the usual way from the above mercury compound by the action of hydrogen sulphide. When recrystallised from hot water it appeared as pale yellow needles melting at 117–18°. (Found : C, 53·2 ; H, 4·8 ; $C_{10}H_{11}O_5N$ required C, 53·3 ; H, 4·9%.) The compound was easily soluble in all the common organic solvents and was quite stable in the presence of dilute mineral acid and alkali solutions over long periods.

4. On orthonitrocinnamic acid. Anhydride of α-hydroxymercuri-β-methoxy-2-nitrocinnamic acid.—*Ortho*-nitrocinnamic acid is rather sparingly soluble in cold methyl alcohol and consequently there was no reaction with mercuric acetate in the cold probably due to the low concentrations of the reactants. However on boiling the nitrocinnamic acid with excess of mercuric acetate in methyl alcoholic solution for about 30 hours, a good yield of the addition product (anhydride) was obtained. In this case also the first precipitate was filtered off and discarded. The substance decomposed at 215°. (Found : Hg, 47·5 ; N, 3·5 ; $C_{10}H_9O_5HgN$ required Hg, 47·4 ; N, 3·3%.) It behaved quite similar to the *meta*-nitro-compound.

β-Methoxy-2-nitrodihydrocinnamic acid obtained from the above compound crystallised from hot water as yellow rectangular plates melting at 151–52° and was very similar to the 3-nitrocompound in behaviour. (Found : C, 53·6 ; H, 5·0 ; $C_{10}H_{11}O_5N$ required C, 53·3 ; H, 4·9%.)

Summary.

The action of mercuric acetate on cinnamic acid, *p*-methoxy and *o*- and *m*-nitrocinnamic acids in methyl alcoholic solutions has been examined.

In general they form at first the mercuric salts which subsequently undergo further change. With cinnamic acid there is no mercuration of the benzene ring; only addition at the double bond takes place and the product has the anhydride form. In the cold *p*-methoxycinnamic acid undergoes mainly addition whereas on heating with excess of the reagent two acetoxy-mercuri groups further enter the nucleus. The compound has a free carboxyl group. The nitrocinnamic acids do not undergo mercuration; they form addition compounds only on heating and these have the anhydride structure. All the methoxymercurials yield β-methoxydihydrocinnamic acids on treatment with hydrogen sulphide and they are found to be stable in the presence of cold acids and alkalis.

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